MARTIN MARIETTA

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MARTIN COMPANY

INTERMOLECULAR BONDING OF VARIOUS METALS AND ALLOYS BY THERMOCHEMICAL VAPOR DEPOSITION

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ABSTRACT

This four phase feasibility study was directed toward the intermolecular bonding of various metals and alloys by thermochemical vapor deposition at temperatures below the metals and alloys recrystallization temperature. The alloys studied were aluminum alloy 2219-T87, stainless steel alloy 321, titanium alloy 8Mo-1V-1Co, and beryllium.

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SUMMARY

A program of four phases was directed toward the intermolecular bonding (welding) of various metals and alloys by thermochemical vapor deposition (TCVD) at temperatures below the metals and alloys recrystallization temperature. This feasibility study resulted in the development of techniques for joining the following:

Phase I — Joining aluminum alloy 2219-T87 with TCVD aluminum from the thermochemical vapor decomposition of tri-isobutyl aluminum in a temperature range of 400 to 500°F.

Phase II — Joining stainless steel alloy 321 with TCVD nickel-iron-carbon alloys from the simultaneous thermochemical vapor decomposition of nickel and iron carbonyls in a temperature range of 400 to 800°F.

Phase III — Joining titanium alloy 8Mo-1V-1Co from TCVD of suitable inorganic or organic thermochemical vapor decomposition compounds in a temperature range of 400 to 700°F.

Phase IV — Joining beryllium alloys from TCVD of suitable inorganic or organic thermochemical vapor decomposition compounds in a temperature range of 400 to 800°F.

Phase III was later cancelled with the time allocated to an extension of the Phase II effort. Phase IV was only a theoretical state-of-the-art study to determine the feasibility of using thermochemical vapor decomposition techniques for joining beryllium alloys.

In Phase I, actual weldments by aluminum joining were not achieved; however, further development of the process should be made considering the chemical and metallurgical quality of the thermochemical vapor deposited aluminum and its interface bond with the substrate.

In Phase II stainless steel joining, acutal weldments were achieved, exhibiting impact toughness and tensile strengths of 40,000 psi. The Ni-Fe-C TCVD alloys developed indicate potential available strengths exceeding 100,000 psi.

Phase II in particular established the bulk of the TCVD mechanisms necessary for the fabrication of weld joints. These mechanisms (surface preparation, specimen joint geometry, Ni-Fe-C alloy development, and grain morphology) could be used at this level of development to readily form the Phase I aluminum joints if time permitted. The Phase II development also established the TCVD mechanisms for Ni-Fe-C alloy depositions, providing both the techniques and the alloys necessary for making structural welds at temperatures below the recrystallization temperatures.

This process, when fully developed, should find application in the repair and fabrication of orbiting space platforms and space vehicles as well as in situations where conventional welding temperatures cannot be tolerated.

INTRODUCTION

While the design of space-age vehicles is limited by the capabilities of available structural materials, the joining of these materials presents a more serious problem. Design and manufacturing techinques frequently preclude the use of fasteners such as rivets while welding temperatures change the metallurgy of the metal being joined and brazing introduces discontinuities in the structural system. Ideally a method of joining metals will have no effect on the base metal and will produce a weld deposit metallurgically identical to or compatible with the base metal.

Conventional welding methods normally require bulky equipment and temperatures high enough to melt the metals to be joined. This melting and the subsequent solidification, phase changes, and non-uniform heating and cooling often result in welds with metallurgical defects, mechanical defects, and residual stresses that may lead to unsuspected premature failure of reduced strengths.

Recently the Martin Company demonstrated the feasibility of joining tungsten using a TCVD process. When tungsten is welded by conventional methods it becomes brittle and low strength welds result; however, weldments produced from the TCVD process are ductile and of high tensile strength, nominally, 135,000 psi.

The TCVD process for welding tungsten is quite straightforward, requiring simply the impinging of gaseous hydrogen and tungsten hexafluoride on the surfaces to be joined. Tungsten deposits as a weld only on those portions of the parts to be joined which have been suitable heated. The deposition reaction proceeds as follows

$$WF_6 + 3H_2 \xrightarrow{\Delta} W + 6\ HF$$

The temperature required to initiate this reaction (875°F) is quite low when compared with that required for conventional welding (6140°F).

With this background, the subject four-phase program was developed in which the feasibility of using TCVD techniques for joining other metals was to be determined. The metals selected for this feasibility study are

Phase I Aluminum alloy 2219-T87
Phase II Stainless steel alloy 321
Phase III Titanium alloy 8Mo-1V-1Co
Phase IV Beryllium alloys (state-of-the-art study)

Phase III was later cancelled with the time allocated to an extension of the Phase II study.

I. TECHNICAL APPROACH

An ideal TCVD joining process should be capable of meeting many basic considerations (Figure 1) however, the following four considerations are of prime importance:

1. Process time for fabricating the joint should be short

2. Process joints should yield strengths and ductility equal to or exceeding that of the members being joined

3. Process itself should possess excellent microthrowing power, i.e., the ability of the TCVD deposit to project itself into sharp corners or in recesses and the capability of bridging gaps between the members to be joined

4. Process temperatures should be well below the substrate members recrystallization temperatures.

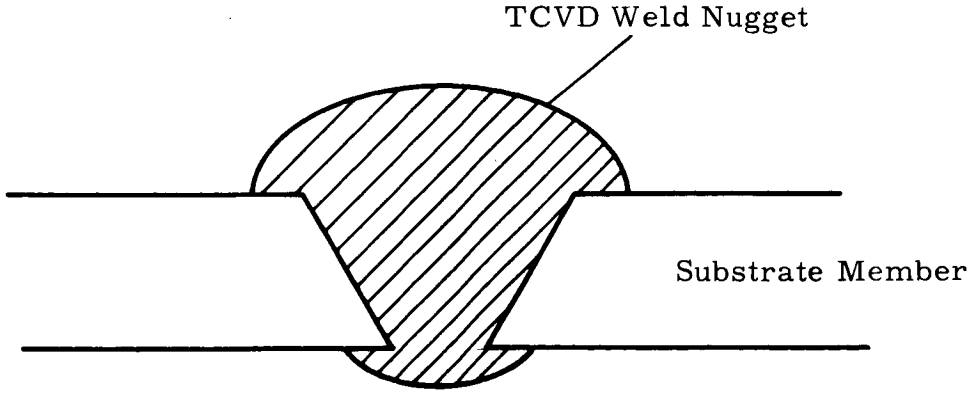


Figure 1. Typical TCVD Weldment

The organometallic compounds appear to be the most suitable for meeting these conditions, particularly with respect to recrystallization temperatures. Refractory metals (tungsten, tantalum, columbium, molybdenum) have a comparatively high recrystallization temperature allowing the use of both inorganic (halides such as fluorides, chlorides, bromides, and iodides) and organometallic TCVD plating materials. The less refractory metals (aluminum, stainless steels, titanium, beryllium) have much lower recrystallization temperatures thus limiting TCVD plating material selection almost strictly to the organometallics such as tri-isobutyl aluminum (TIBA) for joining aluminum and the carbonyls of nickel and iron for joining stainless steels.

Two factors are important in the selection of suitable organometallic thermochemical vapor deposition plating compounds·

1 The ability to yield thick deposits suitable for weldment nuggets

2 Microthrowing power. (Where limitations exist, various process techniques such as flow rates, nozzle design, joint geometry design, etc., are used to compensate in order to obtain a structural joint.

The design requirements for structural joints are presented below:

1 Engineering Considerations

a Strength equal to or exceeding that of the members being joined

b Toughness (ductility) to resist impacts, thermal cycling, thermal shock, etc.

c Metallurgical electromotive compatibility to resist galvanic corrosion

d Metallurgical stability over service operating temperatures.

2 Metallurgical Considerations

a Adhesive strength - metallurgical bond, i.e., some mutual metal solubility of the TCVD deposit and the substrate without the formation of (detrimental) low melting point phases, brittle metallics, compatible coefficient of expansions

b Cohesive strength - high density, fine grain structure of controlled purity, uniformity; free from voids and/or microcracks.

The TCVD process evaluation objectives (Figure 2) are listed below:

1 TCVD Plating Materials

a Readily vaporized, metered, and transported from plating generators, through process lines, nozzles . . . to the joint area.

b Possess decomposition products which are gaseous, easily analyzed, and uncomplicated by side reactions.

c Decompose over a short range of temperatures and produce a pure deposit, especially control of codeposited carbon.

d Undergo thermal decomposition without chemical reaction with the substrate, e.g., sulfur or phosphorus TCVD compounds could embrittle the stainless steel.

e Nontoxic, easily analyzed, high-purity, low cost.

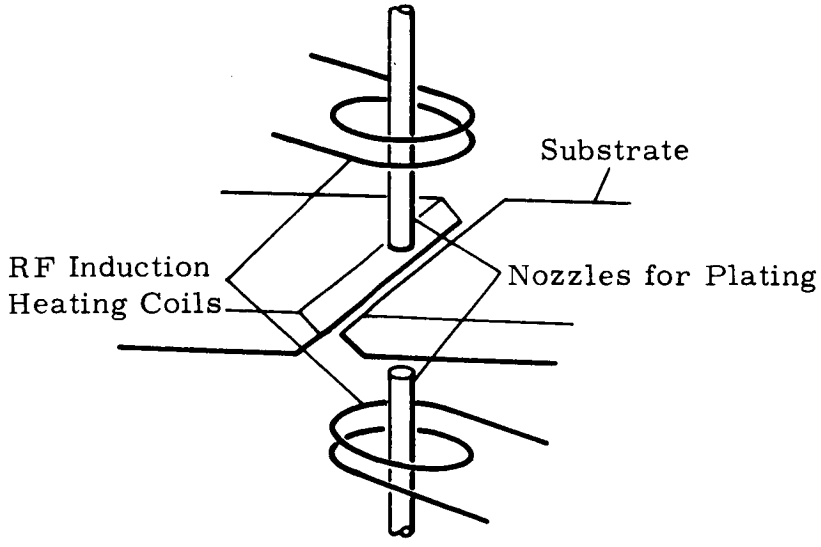


Figure 2. TCVD Process Evaluation

2 Engineering Considerations

a Strength

b Toughness

c Galvanic corrosion resistance

d Metallurgical stability.

3 RF Induction Heating

Localized uniform heat to confine weld deposit to joint, i.e., control of hot and cold spots which cause TCVD defects such as nodules, craters, plateau, voids, etc.

4 Environment

a Vacuum - Suitable for treatment of substrate, i.e., 10^{-4} torr or better

b Purity - Freedom from sulfur, phosphorus, H_2O, and O_2 which foul or embrittle substrate; preferably 10^{-6} torr or better H_2O dew point -100°F maximum; O_2 less than 1 ppm.

5 Substrate Cleaning

Suitable for metallic bond to TCVD deposit, i.e., free from

a Organics contaminants - grease, oils, moisture

b Inorganic contaminants - oxides

c Gases adsorbed on surface.

6 Nozzles

Nozzle configuration and angle to provide

a Laminar uniform flow over joint to avoid turbulence

b Confine weld to joint area.

7 Joint Geometry

The joint geometry must be suitable to allow the full throwing power of the plating compound, i.e., must have free entrance and exit.

Poor Good

Typical Joints

Preferred

Butt Single Bevel Double Bevel

The TCVD of thick coatings from organometallic plating compounds is invariably complicated by the codeposition of carbon. For metals such as iron (Fe), the codeposition of carbon presents a difficult obstacle because the TCVD deposits are exceedingly birttle (unsuitable for weld nugget thickness). Metals such as nickel are not adversely affected by codeposited carbon and thick coatings can be successfully deposited, but the TCVD deposit remains soft and therefore of low strength unsuitable for structural weldments.

The codeposition of both nickel and iron simultaneously under controlled process parameters appeared to offer a technical solution to the dilemma of choosing between brittle, high strengths weldments or tough, low strength weldments.

After deciding upon the coating thickness mechanism, the problem of microthrowing power soon became apparent during initial process weldment attempts. Substrates with macro or micro effects and substrates with holes propagate their defects or holes through the TCVD deposit (Figure 3). TCVD deposit microsections show microholes, microcracks, and voids all originating from defects in the substrate. Since a joint displays a dimensional gap, the TCVD, still displays a microgap even though the deposit is an inch thick. (Microsections of these joints shows the TCVD gap constantly reducing, perhaps, all the way to a void of atom size.) Such weldments are of very low strengths and are completely unsuitable for structural designs.

Microthrowing power presents a formidable problem, with respect to joining, because of the tendency of the substrate joint gap to initiate a

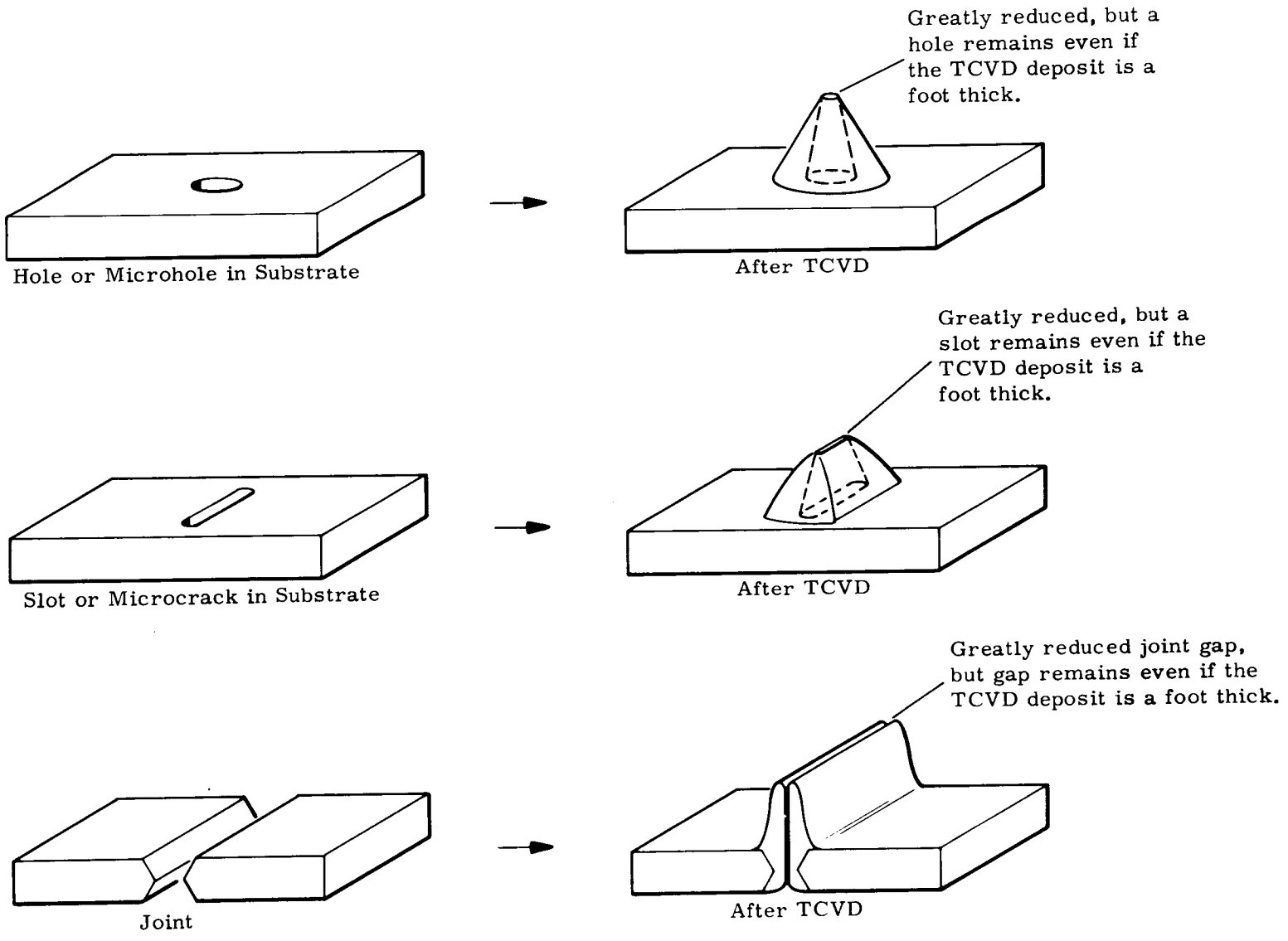


Figure 3. Microthrowing Power of TCVD

microcrack throughout the TCVD deposit. Similar to the process of electroplating, the problem of microthrowing power is solved best by the simultaneous considerations of the following factors:

1 TCVD plating compound characteristics

2 Plating system environment (contamination control)

3 Substrate material

4 Substrate joint geometry

5 Substrate heating method

6 Process control - vapor generation, flow, and control

7 Process procedures.

Each one of these factors will be analyzed in detail in respect to microthrowing power as well as other technical problem areas.

A. TCVD PLATING COMPOUND CHARACTERISTICS

In addition to the engineering, metallurgical, and process considerations previously stated, a separate analysis of each metal to be joined (aluminum, iron and steel, titanium, and beryllium) and the mechanics of the TCVD reaction will be examined.

1. Basic Considerations

a. Joining of Aluminum

The deposition of aluminum on ferrous and refractory metals is a well developed process. The commercial processes for aluminizing, commonly called calorizing, forms tenacious aluminum coatings. In these processes, the deposition of the aluminum depends on the thermal-hydrogen reduction of trihalides in the temperature range of 1100 to 1800°F and proceeds as follows:

$$2AlX_3 + 3H_2 \xrightarrow{\Delta} 2Al + 6HX.$$

The high temperatures required preclude the use of this reaction for the deposition of aluminum on aluminum and its alloys as a welding process, because the temperatures are in the melting point range of aluminum alloys and thus, would defeat the purpose of this program.

Recently aluminum coatings have been deposited at reasonably low temperatures in the range of 500°F by the thermal decomposition of organometallic compounds such as tri-isobutyl aluminum. This reaction proceeds as follows:

$$(C_4 H_8)\ Al \overset{\Delta}{\rightarrow} Al + 1\tfrac{1}{2} H_2 + 3(C_4 H_8).$$

The metallurgical quality of the deposited aluminum is excellent and the prognosis for adapting this or similar reactions for the production of joints in aluminum is excellent.

b. Joining of Stainless Steel

Several reactions which may be used in a joining process, have been used for the deposition of iron. These reactions include the reduction of ferric chloride with hydrogen at 1200°F, thermal decomposition of ferrous iodide in vacuo at 2010°F, and thermal decomposition of iron carbonyl. A comparison of the advantages and disadvantages of several TCVD iron plating compounds was made and the results favored the 600°F TCVD of iron pentacarbonyl (Appendix B). Resultant depositions contain a minimum of 0.7 percent carbon codeposited with the iron. The deposits were brittle but low temperature hydrogen reductions offered the possibility of restoring ductility. (This was not the case since the reductions required 1000°F temperatures for many hours for every few thousandths of deposition).

Nickel presents a unique situation. Nickel carbonyl TCVD deposits nickel readily at 400°F in an adherent, ductile form. Above 400°F finely divided nickel is formed which catalyzes the disproportionation of CO, causing carbon to codeposit with the nickel. The carbon, however, does not affect the mechanical properties of the nickel as it does with the iron.

Nickel can also be deposited at 662 to 842°F (350 to 450°C) from nickel acetylacetonate vaporized at 320°F (160°C), preferably at reduced pressure.

With respect to the making of a high strength, impact resistant, structural joint, neither iron nor nickel from the TCVD of their carbonyls yields a suitable deposit. The iron deposits are intrinsically of high strength but brittle while nickel deposits are ductile but of low strength. Simultaneous deposits of both iron and nickel, under controlled TCVD processing, yields Ni-Fe-C alloys suitable for structural joining (welding).

Nickel and iron are metallurgically compatible with the 321 stainless steel substrate (carbonyl plating compounds are free from sulfur and phosphorus which embrittle stainless steel) and are also free from free

oxygen which would oxidize the surface of the stainless steel. TCVD carbon from the TCVD Ni-Fe-C deposition is prevented from making intimate contact with the stainless steel by use of an initial pure nickel deposit followed by the Ni-Fe-C alloy TCVD.

c. Joining of Titanium

Advances in titanium technology have provided several reliable methods of deposition of the metal and its alloys. For the highest purity and ductility, the deposition of titanium by thermal decomposition of the iodides is recommended. However, reduction of tetrabromide by hydrogen may provide a simpler process. The organometallics with their much lower decomposition temperatures are preferred since the lower temperatures tend to affect less the metallurgical history of the base metal.

As stated earlier the Phase III effort, joining of titanium, was cancelled with the time allocated to the Phase II, joining of stainless steel, study.

d. Joining of Beryllium

Perhaps the most difficult joining problems can be expected with beryllium because it cannot be deposited rapidly or efficiently by any known method. The attendant difficulties are attributable to the stability of berylliums halides, low melting point of the metal (2332°F) relative to the deposition temperature, and the appreciable vapor pressure developed at normal deposition temperatures. Moreover, working with beryllium is hazardous because of the high toxicity of both the metal dust and its oxides. Since the oxides form berylliosis when assimilated, even in minute quantities, special precautions must be exercised.

Van Arkel (Reference 1) deposited beryllium from beryllium iodide vapor by hydrogen reduction at 1472°F. The deposits, however, were badly contaminated with silicon as a result of reaction with the glass reaction chamber apparatus. Hackspell and Besson (Reference 2) reported satisfactory deposits from the hydrogen reduction of beryllium chloride at 1832 to 2732°F. A number of investigators have reported the deposition of beryllium by thermal decomposition of its di-iodide in vacuo at 1292 to 1650°F. However, as with the work of Van Arkel, contamination with silicon and boron was reported, probably from the same source. The Martin Company feels that selection of suitable organometallic materials for the TCVD will eliminate this difficulty. The iodide reactions seem to offer the most promise for the production of weldments in beryllium. However, from the state-of-the-art literature search, it was found that a large number of organometallic beryllium compounds have been synthesized. Such beryl-

lium organometallics could yield beryllium metal at TCVD temperatures much lower than that required for beryllium halides.

2. Detailed Considerations as Related to Microthrowing Power

Nickel and iron carbonyls undergo thermochemical vapor depositions liberating large volumes of carbon monoxide gas, as shown in Figure 4. The overall effect of large volumes of carbon monoxide molecules flowing countercurrent to the fresh carbonyl vapor flow is to seriously limit the ability of the fresh carbonyl vapors to penetrate the hole. Thus the tendency of the deposit is to fill over the hole with a smaller hole remaining at the top. Nine molecules of carbon monoxide gush out of the microhole for each atom of Ni and Fe TCVD deposited.

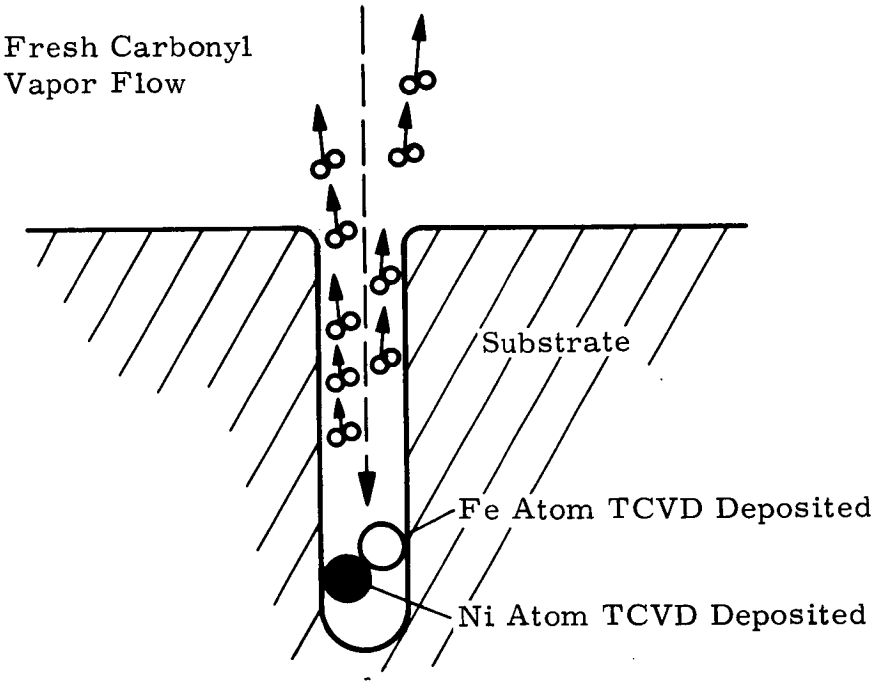


Figure 4. TCVD Deposition versus Microthrowing Power

B. ENVIRONMENTAL CONTROL

The environmental control around TCVD process equipment (Figure 5) is determined by the vacuum and contamination control requirements.

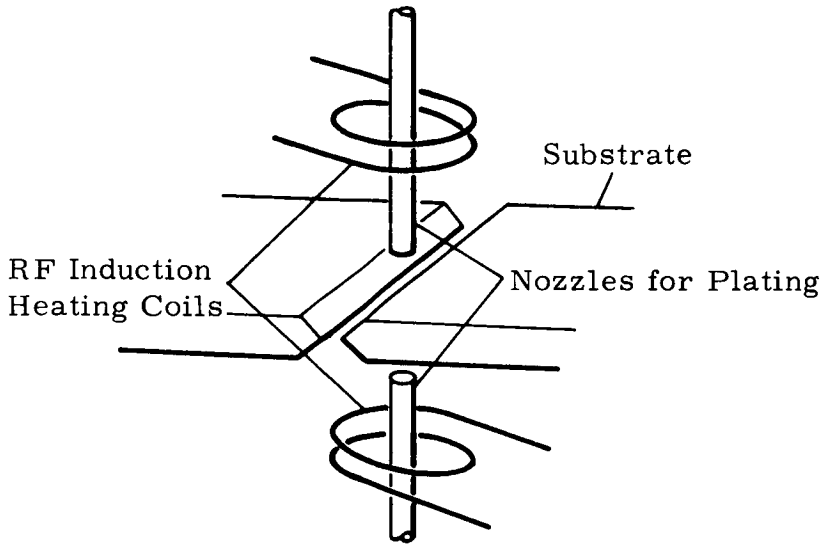
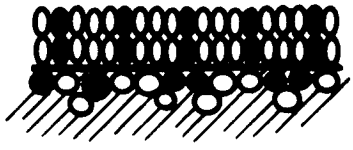


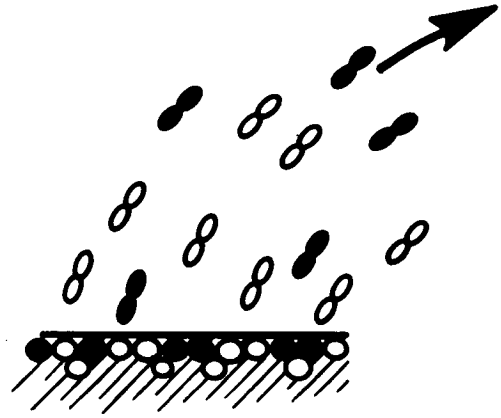
Figure 5. TCVD Environmental Control

1. Vacuum Requirements (10^{-4} torr, minimum)

In addition to adequate cleaning, substrates require degassing to remove absorbed air molecules to obtain metallurgical bonding.



Substrate surface chemically cleaned of oil, grease dirt, oxides, etc. Sketch shows adsorbed air and moisture molecules.



Degassed surface, baked at 800°F at 10^{-4} torr. Sketch shows atoms of chromium, nickel, and iron exposed at surface with no adsorbed gas residues.

2. Contamination Control Requirements

In addition to the vacuum requirements for degassing the substrate, environment contamination, including air leaks, carrier gases, and outgassing, must be controlled to prevent repassivation (particularly activated stainless steels) or embrittlement, as follows:

1 Moisture: dew point of -100°F maximum

2 Oxygen to 1 ppm maximum*

3 Complete exclusion of detrimental elements such as sulfur or phosphorous (embrittle stainless steels)

4 Carbon deposition control particularly on non-stabilized grades of stainless steel.

C. SUBSTRATE MATERIAL

The metal-metal oxide equilibrium in hydrogen atmospheres (Figure 6) clearly indicates the problem of activating and maintaining clean, oxide-

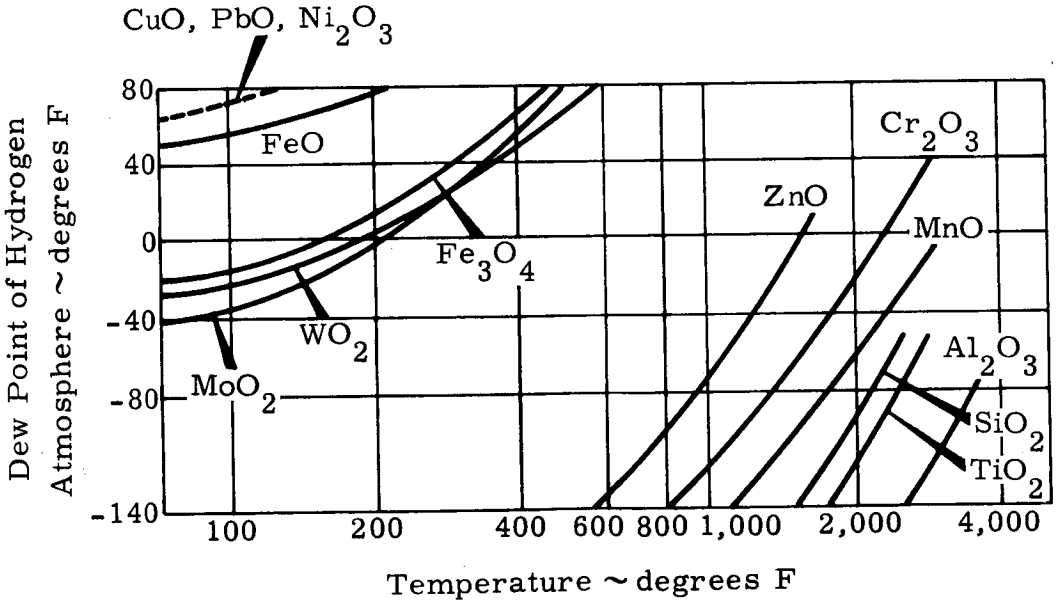


Figure 6. Metal-Metal Oxide Equilibriums in Hydrogen Atmospheres

*Stainless steels activated and nickel electroplated require less stringent environments: e.g., O_2, 2 ppm max; moisture, -60°F dew point max.

free metal surfaces necessary for achieving metallurgical bonding to the TCVD deposit (Figure 7).

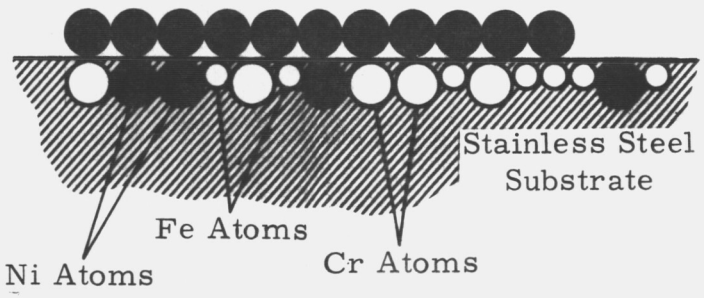


Figure 7. Stainless Steel Substrate

The metal oxides of iron, copper, lead, nickel, and even molybdenum and tunsten are vastly more easy to reduce at low temperatures and at high dew points than zinc, chromium, manganese, silicon, titanium, and aluminum (Reference 3). The element chromium makes hydrogen reduction activation of stainless steels impractical with respect to TCVD objects, i.e., activation requires heating the substrate to high temperatures (1800°F) using palladium purified hydrogen to control oxygen contamination to 1 ppm, maximum, and moisture control to a dew point of -75°F maximum. The temperature of 1800°F approachs the annealing temperatures of the stainless steel substrate.

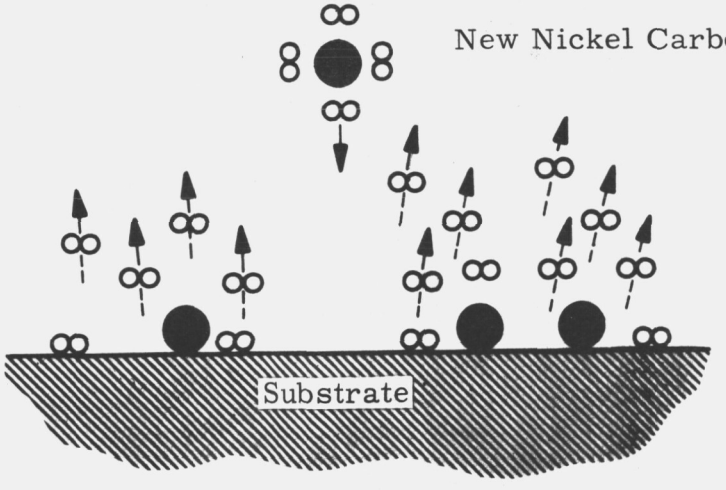
From Figure 6, nickel however is comparatively easy to reduce by heating to 800°F in hydrogen, dew point of -40°F or better. (Moisture control to dew points on the order of -100°F require extra care in process control: baked system chamber and process lines, efficient dessicants, liquid nitrogen cold traps, etc.) The best approach, therefore, is to activate and electroplate the stainless steel with a soft, ductile nickel (such as from a nickel sulfamate bath) to approximately 0.00005 inch thick. Nickel oxide films forming on the electroplated nickel are easily reduced by hydrogen gas treatment at 800°F, in vacuum (the temperature ordinarily used for degas treatments).

Trying to hydrogen reduce the refractory oxides of aluminum, titanium, and chromium (stainless steel) would expose the substrate to temperatures far exceeding recrystallization temperatures and exceeding even melting

point temperatures. By reverting to electroplating procedures, metals such as aluminum can be plated with a thin protective film of tin or zinc; stainless steels can be nickel electroplated, titanium by other suitable methods. The protective film selected should form either no oxides or be easily reduced with hydrogen at low temperatures. The films should meet overall joint objectives (Figure 1) to be metallurgically compatible both to the TCVD deposit and the substrate. Such TCVD weldments must be carefully evaluated. As in Phase II where several types of electroplated nickel were examined. Although all electroplated nickels are metallurgically compatible with both the stainless steel substrate and the TCVD Ni-Fe-C alloy deposit, various nickel electroplates can display deposits ranging from very soft to exceedingly brittle (the latter being unsuitable for joints requiring ductility because weldment would fail at the brittle electroplating film interface during flexure).

D. SUBSTRATE JOINT GEOMETRY

The steps required in the formation of a thermochemical vapor deposition to a substrate are shown in Figure 8 . The illustrations in this section incorporate the organometallic carbonyls of nickel and iron as examples. Other organometallics TCVD react similarly and also consist of the metal atom and some gaseous, removable, by-product.



Legend:

● = Nickel Atom

∞ = Carbon Monoxide (CO) Molecules from Previous TCVD's. i.e.:

$$Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO$$

Figure 8. TCVD of Nickel Tetracarbonyl

TCVD chemical kinetics are affected by the following four mechanisms:

1 Bringing of the nickel carbonyl together with the substrate

2 TCVD reaction at substrate surface to liberate metal atoms of nickel and gaseous CO molecules: $Ni(CO)_4 \overset{\Delta}{\rightleftharpoons} Ni + 4CO$

3 Removal of CO molecules from substrate surface

4 Controlled interdiffusion of fresh nickel carbonyl vapors through the field of CO molecules being removed from the substrate.

In most instances the kinetic controlling mechanisms are determined by steps 3 and 4, i.e., the gas molecules are strongly adsorbed to the substrate surface, making subsequent TCVD difficult. Note also in the simultaneous TCVD of both nickel and iron, the large amount of carbon monoxide molecules liberated, i.e., nine molecules of carbon monoxide for every atom of Ni and Fe deposited.

The carbon monoxide causes two real problems: 1) an adverse effect on the metallurgical bond (poor adhesion) and 2) serious throwing power deficiency necessitating design of the joint geometry.

In the metallurgical bond problem (Figure 9) some of the carbon monoxide molecules escape but others are caught at the deposition surface. TCVD nickel continues to build up on the adsorbed carbon molecules resulting in a low strength, low density carbon monoxide-nickel interface which subsequently loses adhesion to the substrate, i.e., blisters and peels from the substrate.

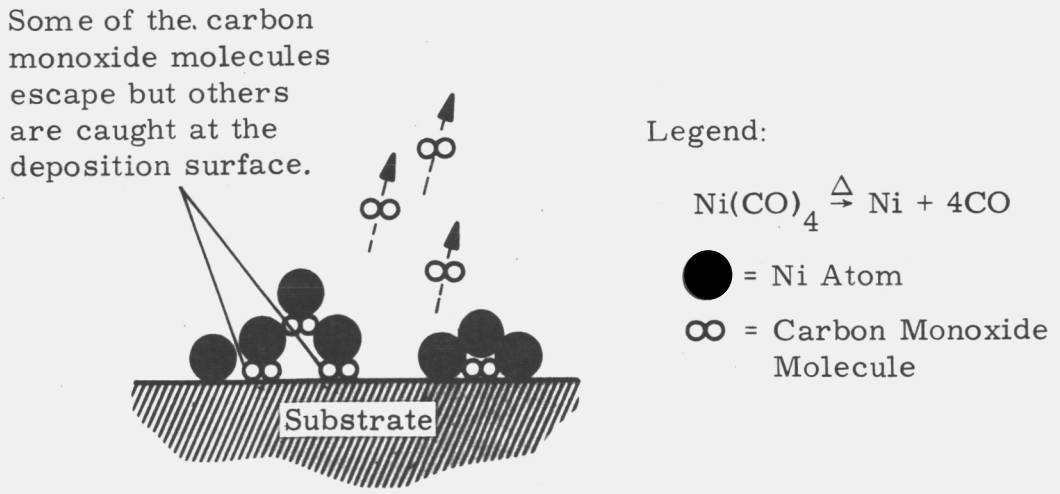


Figure 9. Metallurgical Bond Problem

This problem is corrected by first degassing the substrate free of adsorbed air molecules; depositing a TCVD nickel flash plate approximately 0.00005 inch thick; and degassing again to remove the carbon monoxide molecules adsorbed at the TCVD deposited/substrate interface. For technical purposes, the TCVD process should be interrupted frequently for carbon monoxide molecule degassing but in practice this is accounted for by the use of as high vacuums and temperatures as possible and still be within the TCVD engineering design limits of low temperature substrate exposures.

The second problem (Figure 10) is even more acute. Carbon monoxide molecules can leave the nickel atom site via many directions. Actually many nickel carbonyl molecules are TCVD depositing simultaneously. The large evolution of carbon monoxide molecules greatly crowds the avenues of escape. Still, the illustration is approximately true.

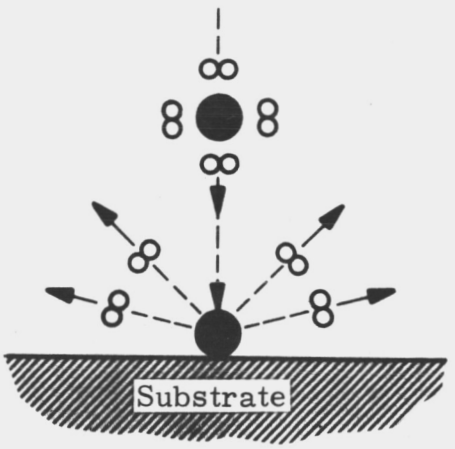


Figure 10. Nickel Carbonyl Molecules TCVD Depositing

Consider, however, the problem of a small hole or microcrack (Figure 11) within the substrate. For every atom of nickel deposited in the hole or microcrack, a 4:1 ratio of the number of molecules of carbon monoxide to nickel carbonyl molecules must come out to allow for the entrance of the next nickel carbonyl molecule. The "gushing out" action of the carbon monoxide makes it difficult for new nickel carbonyl molecules to enter; as a result the microhole does not fill as readily as the top substrate.

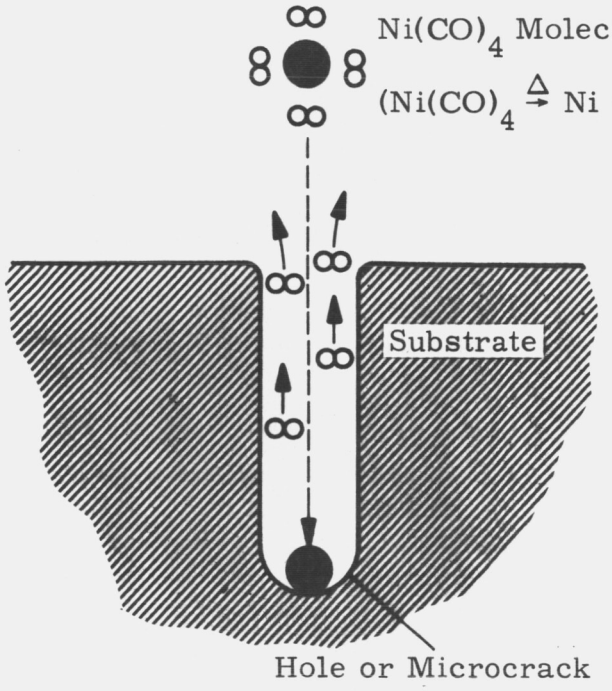
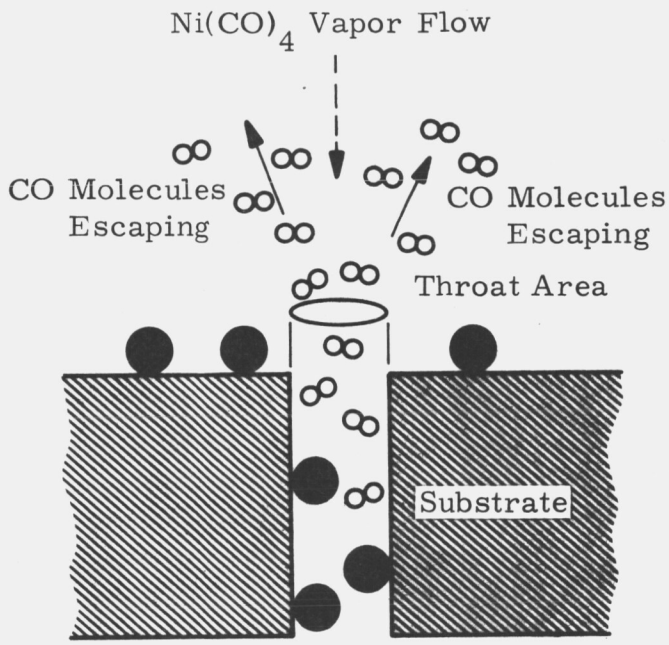


Figure 11. Microcrack Problem

The combination of a large amount of carbon monoxide molecules flowing in a direction opposite to that of the nickel carbonyl molecules, plus the fact that the microcrack offers a large surface area to which these carbon molecules become strongly absorbed, work against the TCVD mechanism reaction filling in the hole or microcrack.

A flat surface is readily TCVD deposited, i.e., carbon monoxide molecules free to escape in many directions, and a gradually curved surface is also readily TCVD coated. However consider the case of a straight butt joint. During the initial deposit (Figure 12) the throat of the butt weld is sufficiently open to allow the escape of the carbon monoxide molecules. In the intermediate deposition stage (Figure 13), similar to the electroplating phenomena, substrate surfaces closest to the TCVD plating material are exposed to the richest supply of TCVD metal atoms and also are in best location for ready loss of carbon monoxide molecules. This results in a rapid build-up of surface edges and a rapid decrease of build-up inside of holes and crevices. Figure 14 shows the crack extending down into the microcrack.

Initial Deposit

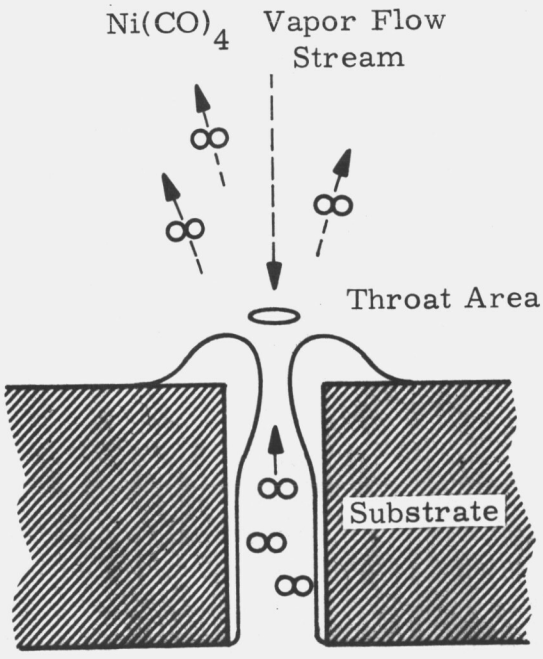


Note: The throat of the butt weld is sufficiently open to allow the escape of the carbon monoxide molecules.

$$Ni(CO)_4 \xrightarrow{\Delta} Ni + 4CO$$

Figure 12. Initial Deposit of Nickel Carbonyl

Intermediate Deposition



Note: Similar to the electroplating phenomena, substrate surfaces closest to the TCVD plating material are exposed to the richest supply of TCVD metal atoms and also are in best location for ready loss of carbon monoxide molecules; resulting in rapid buildup of surface edges and a rapid decrease of buildup inside of holes and crevices.

Figure 13. Intermediate Deposit of Nickel Carbonyl

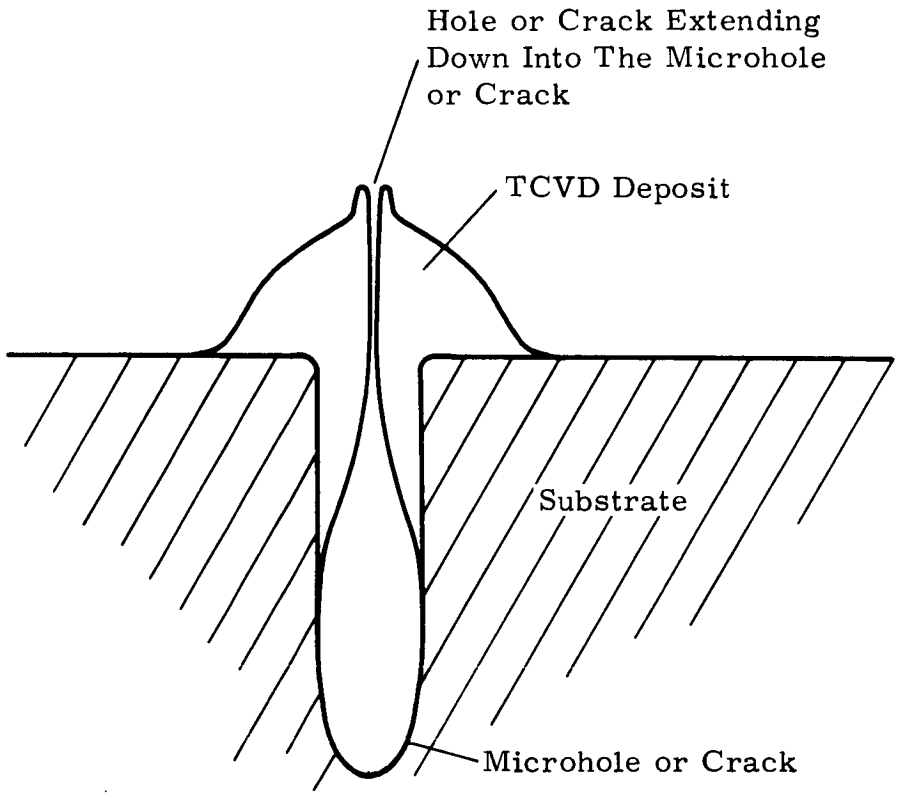
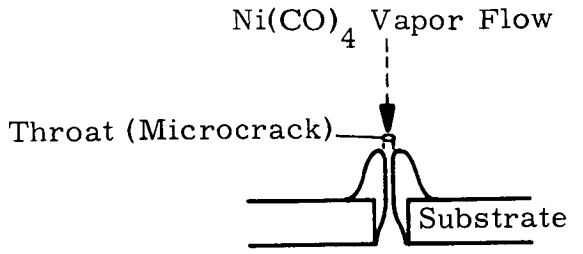


Figure 14. TCVD Microhole or Crack Showing a Smaller Hole or Crack Extending Up Through The TCVD Deposit

Consider a theoretical carbonyl compound where only one carbon monoxide molecule is attached to the metal atom. Under these circumstances a high percent of the TCVD compound would be metal. Subsequent TCVD depositions would have far less carbon monoxide gas "gushing out" of the microholes or cracks, countercurrent to the fresh carbonyl vapor stream. The result would be much better microthrowing power thermochemical vapor deposition plating compound.

In the final deposition stage for a single nozzle (Figure 15), the throat of the butt weld is essentially closed (actually a microcrack) through which passage of fresh nickel carbonyl molecules becomes almost impossible. Where depositions are made on both sides of the joint, i.e., double nozzles (Figure 16), the problem still remains acute. Not only does the microcrack limit the fresh supply of nickel carbonyl from penetrating into the microcrack, but the large volumes of carbon monoxide molecules rushing counter current to the nickel carbonyl molecules hinder depositions (micro-throwing power).

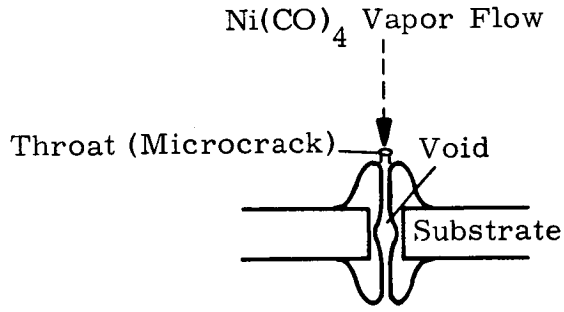
Final Deposition



Weldment, Single Nozzle (Top Side)

Note: The throat of the butt weld is essentially closed (actually a microcrack) through which passage of fresh $Ni(CO)_4$ molecules becomes almost impossible. Where depositions are made on both sides of the joint i.e. double nozzles the problem still remains acute.

Figure 15. Single Nozzle Weldment



Weldment, Double Nozzle (Both Sides) Simultaneously

Note: Not only does the microcrack limit the fresh supply of $Ni(CO)_4$ from penetrating into the microcrack; but the large volumes of carbon monoxide molecules rushing counter current to the $Ni(CO)_4$ hinder depositions (microthrowing power).

Figure 16. Double Nozzle Weldment

To effect structural joints, the configuration must allow ready entrance of fresh nickel carbonyl vapor and free, ready exit of the waste carbon monoxide molecules. Ideally TCVD plating compounds should consist of almost all metal with very little other fractions, e.g., carbon monoxide molecules. Ideally iron carbonyl should be Fe CO (actually it is Fe $(CO)_5$) and nickel carbonyl should be NiCO (actually it is $Ni(CO)_4$).

To deposit one atom of iron and one atom of nickel, nine molecules of carbon monoxide must be withdrawn free from the weld area. Weld joints must be opened-up with various bevels to allow the escape of these carbon monoxide molecules and to readily admit fresh molecules of TCVD plating compounds. As cited by Disckind (Reference 4) "Joint geometries are critical in obtaining sound deposits. High depth to width ratios of butt joint gaps do not appear to be feasible. With depositions from both sides and double V bevels, sound deposits can be readily made."

Typical acceptable and unacceptable simple weld joint geometries are shown in Figures 17 and 18.

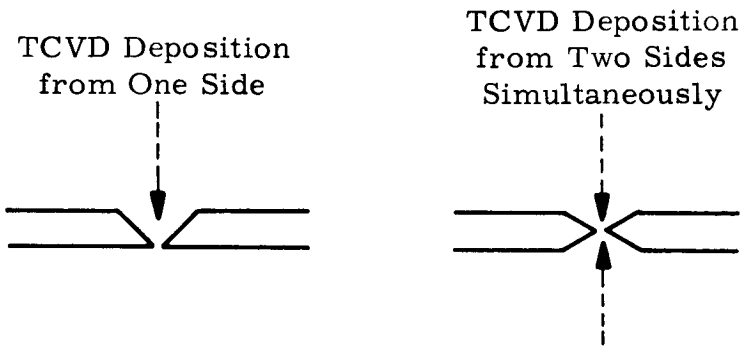


Figure 17. Acceptable Weld Joints

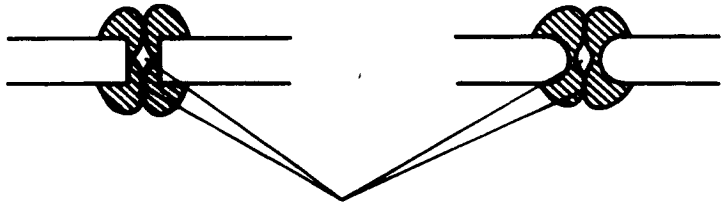


Figure 18. Unacceptable Weld Joints

E. SUBSTRATE HEATING

In general, substrate heating is a straight forward technique but not without problems. Direct resistance heating is not possible since the weld gap (joint) represents an electrical discontinuity. A heating element may be placed in juxtaposition with the substrate thereby heating the substrate by conduction. Other heating methods appear more direct. RF induction heating (too large and heavy for spare work) was used for this contract TCVD work.

The type and location of the heat input is especially important. Most of the previous TCVD have been concerned with coatings (Appendix C). Heat transfer requirements for coatings are comparatively low when compared to a nozzle blowing a fresh stream of the TCVD plating material against a substrate. The heating method selected must be capable of high heat inputs into the highly localized weld area. The same heat input to the entire weld piece would result in excessively high temperatures on other remaining weld substrate members (Figure 19).

F. CARBONYL VAPOR GENERATION, FLOW, AND CONTROL

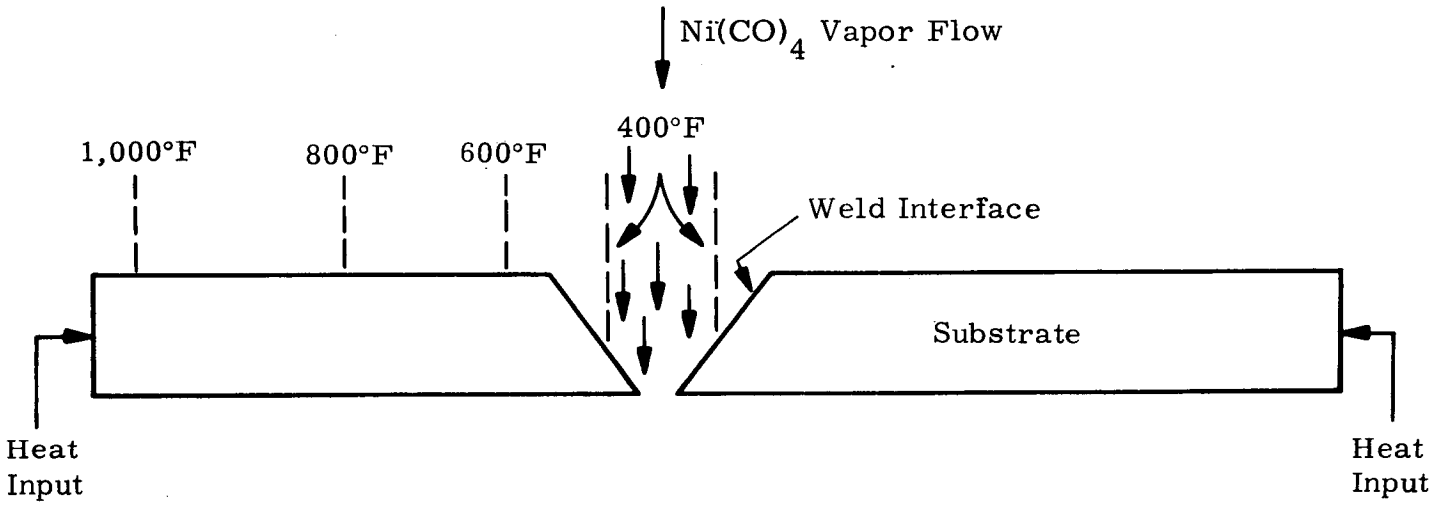
Nickel and iron carbonyls, liquids at room temperatures, are easily vaporized at plating system vacuum pressures of approximately 1/2 mm Hg. Flowmeters are located immediately above the carbonyl generators (Figure 20). Carrier gases are not necessary to transport the carbonyl vapors to the plating chambers since the high vacuum downstream allows the carbonyls to exert their individual vapor pressures resulting in ready flows to the plating chamber. Various noble gases such as helium, argon, or nitrogen, deoxidized and dried, may be used for purging the plating system prior to the TCVD process run. Dry, deoxidized hydrogen is also valuable for reducing nonrefractory oxides of metals such as the electroplated nickel stainless steel substrate.

Organometallic flowrates, nozzle design and configuration, and weld interface temperature control are of prime importance. Flowrates need to be balanced against proper nozzle (orifice) design to give smooth, nonturbulent, laminer flow of the organometallics. Weld interface temperatures are extremely important and tend to run as much as 400°F cooler than the juxtaposition thermocouple area, about 1/8 inch distance.

G. PROCESS PROCEDURE

Substrates to be TCVD joined are formed to an acceptable joint geometry, chemically cleaned, activated (deoxidized), and coated with an atmosphere protective metal film, usually an immersion coating such as a zincate for aluminum, or electroplate such as an electroplate (nickel) for stainless steels. Members are placed in a welding jig and a thermocouple is placed as close as possible to (but not in) the welding interface.

The assembly is placed into the TCVD plating system chamber and degassed at 800°F for at least 15 minutes; plated at 800°F for 30 seconds; then degassed again as before. The entire operation is performed under maximum vacuums, preferably well below 10^{-4} torr (0.1 microns). Moisture and oxygen contamination must be controlled to a degree where reoxidation of the pretreated substrate surfaces will not occur (usually O_2



Note: If a heat input is supplied some distance from the weld interface, temperatures upstream could be much greater, perhaps even exceeding the recrystallization temperature (depending on the thermal conductivity of the substrate, TVCD flowrates chemical energy requirements, etc.).

Figure 19. TCVD Plating Compounds Impinging on Heated Substrate

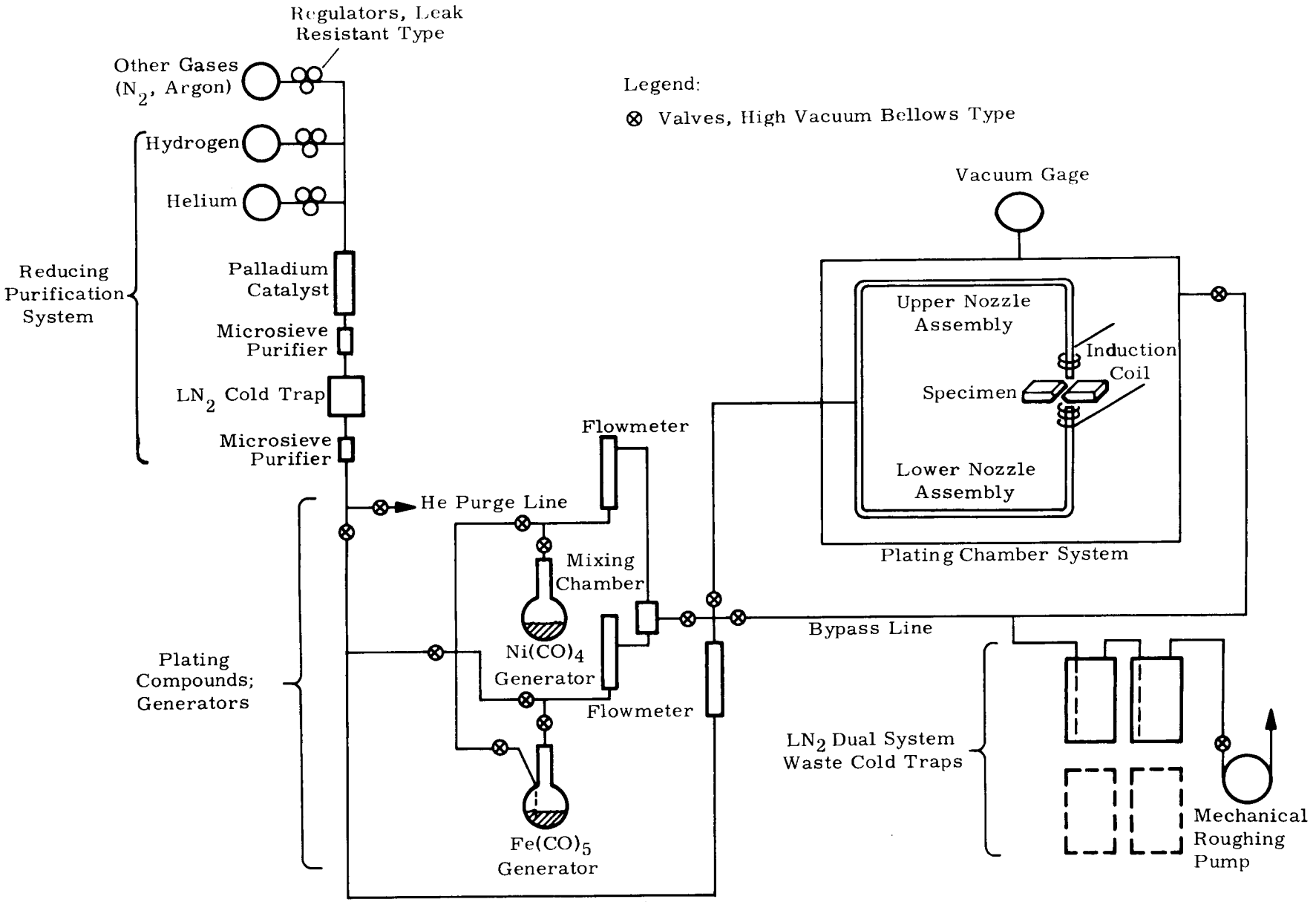


Figure 20. Typical Process Schematic for Alloy Depositions Using Two Organometallics (Nickel Carbonyl and Iron Carbonyl)

< 1 ppm; moisture < dew point of -75°F). Substrate surfaces are flushed continuously during degassing and plating with a palladium purified helium/hydrogen gas mixture dried to a dew point of -75°F). (The He/H_2 mixture serves to reduce metal oxides and also to aid in degassing).

A TCVD Ni-Fe-C alloy is applied over the thin, degassed TCVD deposit (usually Ni) and plated for a time sufficient to build-up a weldment (usually 60 to 90 minutes to deposit 50 to 100 mils). Inch thick coatings can be deposited with little trouble (plating nozzles need to be adjusted, i.e., withdrawn from substrate as TCVD deposit thickness increases). Literature Reference 5 recommends several more such degas treatments where TCVD deposits exceed 0.25 inch. Heat treatments are also recommended to improve the metallurgical bond between TCVD deposit and substrate.

Process shut-down consists of shutting off the TCVD plating generators. The entire plating system is flushed with plant nitrogen to remove residual carbonyls. The RF induction heating is turned off and the specimen cooled to room temperature.

Suggestions and recommendation to the process procedure are presented in the following paragraphs.

1. Substrate

As was shown in Figure 6, some metals such as chromium, titanium, aluminum, form stable, refractory metal oxides that are much too refractory to reduce by standard hydrogen-reduction treatments. (See section I. C.). These oxides are known typically to reoccur when broken, e.g., by sandblasting, in as little time as 1/100 of a second. The initial oxide film continues to grow, rapidly tapering to equilibrium after several minutes (the time period required to transfer clean, joint specimens to the TCVD plating system and to evacuate the plating system).

Sandblasting generally is not recommended because too rough a sand grit may leave the substrate with micro-roughness conducive to voids and/or microcracks growth within the subsequent TCVD deposit. Sandblasting may also leave the ceramic medium embedded into the substrate, impairing adhesion.

2. Vacuum System Pressure

After evacuation of the plating system to at least 10^{-4} torr, air leaks and residual oxygen/moisture contamination must be of a low enough level to prevent reoxidation of thermal hydrogen-reduced, pretreated, substrate

surfaces. The plating system may be flushed with inert gases (or nitrogen) and/or baked. Usually after the system has been thoroughly cleaned of air and moisture, proper operational procedures, keeping the chamber closed and pumped down or filled to atmospheric pressure with dry inert gas such as helium, keep the system operable with a minimum of care. Without the use of a substrate surface pretreatment, oxygen-reactive metals such as aluminum, titanium, and chromium (stainless steels) require exceedingly high temperatures to effect hydrogen reductions and ultra-clean environments, pressures of 10^{-8} torr oxygen 1 ppm, and moisture dew point - 125°F, all minimum. High vacuums are required only during degassing treatments (diffusion pump required). During TCVD plating lower vacuums (mechanical pump only) are used. Diffusion pump oils would quickly become badly contaminated by organometallic plating compounds.

3. Induction Heating

To prevent arcing and corona during induction heating of substrate, an RF stepdown transformer is desirable (voltages inside plating chamber should be under 20 volts) with a minimum number of coil loops, e.g., two loops over specimen, two loops under the specimen, and the center loop grounded to further reduce voltages. Noble gases such as argon, helium, etc. arc and/or corona more than non-noble gases such as nitrogen and carbon dioxide. With respect to TCVD mechanisms both noble and non-noble gases are acceptable, provided moisture and oxygen contamination can be controlled to limits previously stated. Positioning of the specimen within the electromagnetic field requires emf balancing, otherwise one side of the joint will be hotter than the other side. (Initial TCVD filling in the gap tend to arc and burn as the TCVD deposit grows together to become a joint). Substrate materials (aluminum, copper and silver) that do not inductively heat well, because of low electrical resistance to induced currents, require a high electrical resistance such as stainless steel (Figure 21).

As can be seen, the present water-cooled plating nozzle was made by tapping water from the induction coil and electrically insulating each by pieces of heavy-walled vinyl tubing (Tygon). Although this arrangement appeared satisfactory at 10^{-3} torr, it should not be used for systems requiring higher vacuums due to the vinyls tendency toward outgassing.

Induction coils if possible should be placed inside the TCVD plating system. As stated, TCVD organometallic plating compounds tend to metallize interior surfaces (metals, plastics, and ceramics) with a thin film of metal. A ceramic (glass) plating chamber would soon become opaque and should an induction coil be placed outside the (glass) chamber, heating of the (glass) chamber would result.

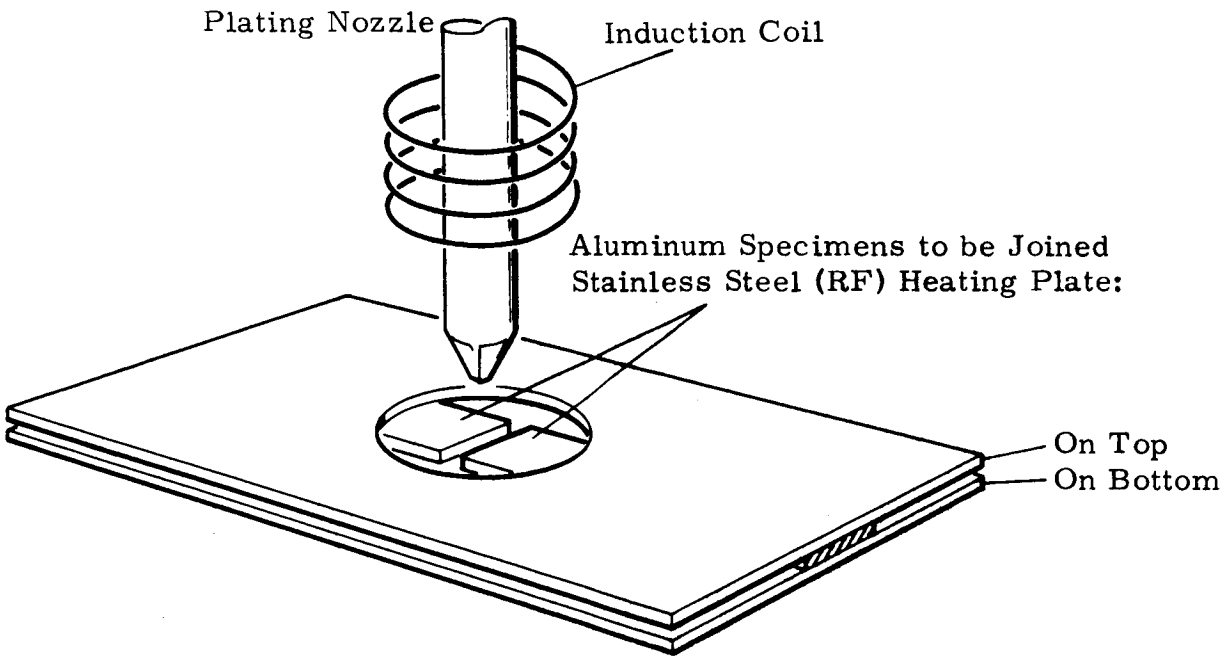


Figure 21. RF Induction Heating of Electrical Low Resistance Metals Such as Aluminum

4. Nozzles

Water-cooled metal, ceramic, or plastic such as Teflon nozzles are satisfactory. With the present TCVD plating system design, the nozzle passes directly through the electromagnetic RF induction field. Although ceramics or plastics do not heat in an induction field, the organometallic TCVD plating compounds do, over a time period, coat process lines including the nozzle with a thin film of metal, even at room temperatures. These metallic films heat rapidly in the induction field, causing further TCVD deposits to quickly plug the nozzle orifice.

5. Cold Traps

Since organometallic TCVD plating compounds tend to readily dissolve in vacuum pump oils, cold traps need to be installed before the pumps to catch the undercomposed TCVD plating compounds (Figure 22). Pump oils, contaminated by organometallics, quickly lose their ability to pump high vacuums and tend to wear close tolerances within the pump (form metal and metal oxide sludges), and also create a toxic health hazard to personnel serving the pumps.

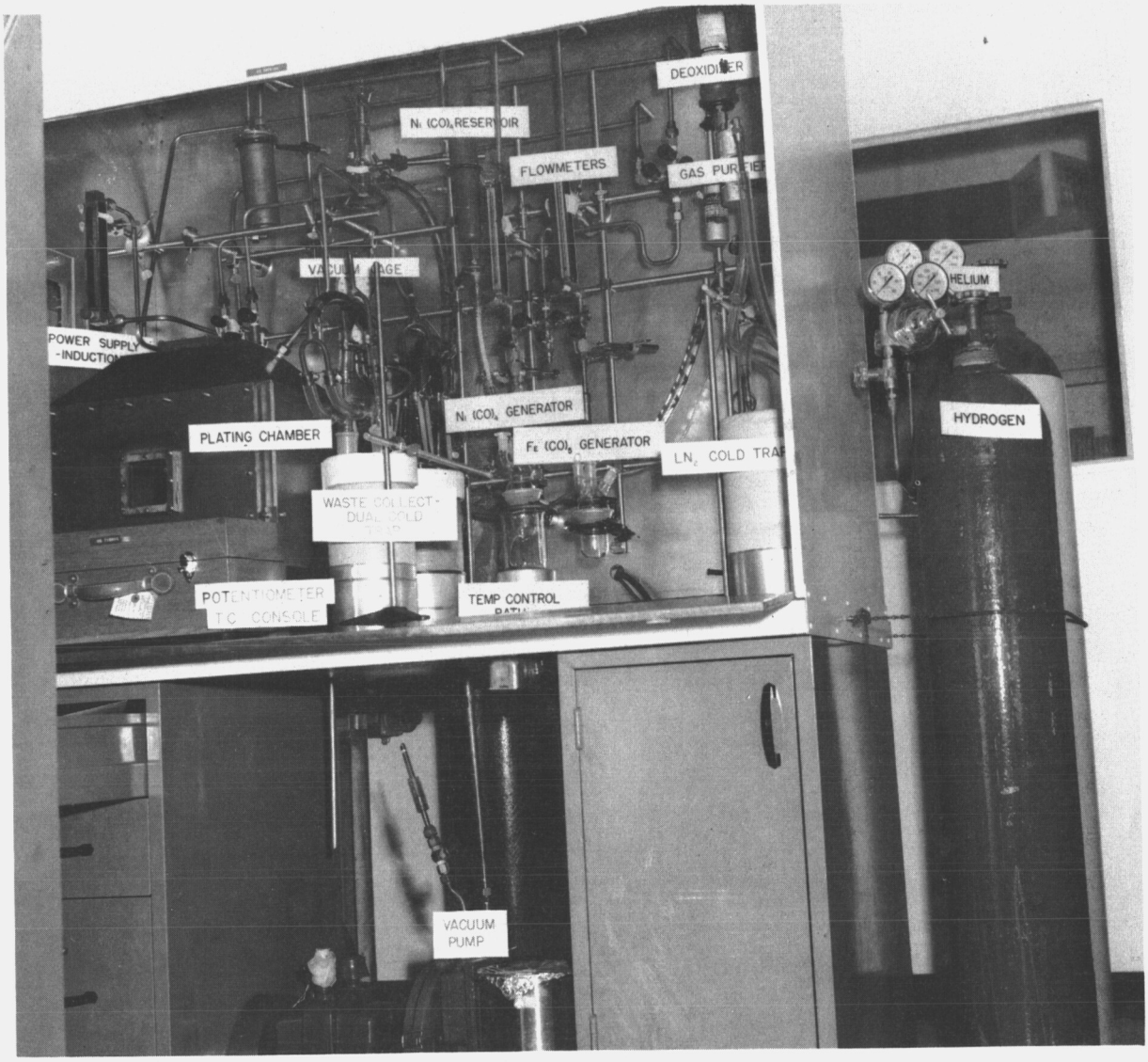


Figure 22. TCVD Apparatus

6. Safety

Typically, TCVD plating compounds are pyrophoric (catch fire spontaneously when exposed to air), toxic, and TCVD decompose at room temperatures not only when exposed to ambient (room temperature) heat but also when exposed to any other form of energy such as light, sound (ultrasonics), radiation, mechanical vibration, etc.

With a suitable cold trap valving arrangement, natural gas can be passed through the cold trap, picking up the waste organometallic vapors, and conducting such vapors to a high temperature (waste) burner. Combustion by-products are comparatively non-toxic.

Ordinarily, organometallics used in vacuum TCVD plating systems present fewer hazardous problems to health since, should leaks be present, leaking will be inward into the system. However for TCVD plating, systems operating near or above atmospheric pressures upmost health precautions (leak-tight system, draft hood, leak-detector alarms, etc.) must be observed.

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II. RESULTS

The research and development conducted indicates a definite feasibility for the thermochemical vapor deposition joining of aluminum, stainless steels, and titanium. High quality TCVD deposits of aluminum (from the organometallic compound tri-isobutyl aluminum) and nickel-iron-carbon alloys (from the simultaneous TCVD of the organometallics compounds nickel tetracarbonyl and iron pentacarbonyl) indicate the feasibility of applying these metals as coatings. Further development work with respect to specimen joint geometry, substrate heating control, and nozzle design extend the coating capability to one of fabrication as structural joints.

Actual weldments were not achieved in the Phase I aluminum joining study. (The reasons for not doing so are described in section III).

Actual high strength weldments were achieved in the Phase II study. Tensile strength values in the order of 40,000 psi were obtained with a Ni-Fe-C alloy of a Rockwell C hardness approximately 40.* Joint tensile strength capability appears to be well over 100,000 psi with higher Rockwell C hardness Ni-Fe-C compositions and improved substrate preparation (See section III).

Phase III was not investigated, and the time was allocated to the Phase II study. The TCVD of titanium presents an unusually difficult technological problem: titanium vapors display an extreme "gettering" action on all except the noble gases.

Subsequent vacuum plating systems require the utmost control of environmental contaminants not only with the more obvious gases, oxygen and water vapor, but with nitrogen and hydrogen as well. Recently, the

*Tensile failure at 40,000 psi occurred between the substrate and the TCVD Ni-Fe-C alloy deposit. The stainless steel substrate had not been pretreated (i.e., nickel electroplated) and had picked up a heavy chromium oxide film during the 800°F degassing treatment.

state-of-the-art for titanium TCVD has been developed for coating applications.† By incorporating TCVD techniques from the Phase II study, together with the newly developed titanium TCVD coating methods, titanium joining could be accomplished.

The Phase IV state-of-the-art literature search indicates that the TCVD of beryllium from the inorganic beryllium halides (fluorides, chlorides, bromides, and iodides) is not feasible with TCVD joining objectives because temperatures exceed the recrystallization temperature of beryllium. The recent development of many beryllium organometallics does offer new, low TCVD temperature possibilities for beryllium metal depositions.

Beryllium vapors, in addition to titanium vapors, display a "gettering" action toward the non-noble gases within the plating system environment. High vacuum techniques with close contamination control of O_2, N_2, H_2, H_2O would be similarly required.

This feasibility study resulted in the development of many new joining techniques. As discussed in detail in the section I, TCVD deposits tend to be either too hard and brittle (tend to exfoliate and spall) or too soft (tend to be of low structural joint strength). A new group of TCVD Ni-Fe-C alloys were developed and tested, indicating an application suitability for a wide range of engineering services including adaptability for TCVD structural weldments. In addition to the alloy development, many joint fabrication techniques were developed extending the use of present TCVD coatings down to joining capability. Techniques developed include TCVD organometallic plating compound analysis with respect to microthrowing power, substrate preparation of chemically reactive metals (aluminum, stainless steels, and titanium), joint geometry analysis, heating methods and control, and process procedures.

†General Technologies Corporation, Alexandria, Virginia

III. DISCUSSION

The thermochemical vapor deposition process shows definite promise for in-space fabrication and repair of space structures and orbiting vehicles. The hard vacuums of outer space remove many of the problems encountered with the process in the earth's atmosphere. For example, oxygen and moisture contamination ceases to be a problem and the liquid organometallic TCVD plating compounds vaporize readily, with boiling points becoming less than 50°F. Cleanliness of surfaces to be joined is of small importance, since in outer space surfaces tend to be self-cleaning. The weight and bulk of the TCVD plating organometallic generator and nozzle required is insignificant; a typical lecture bottle type container is 2 inches in diameter, and 14 inches long, and weighing only about 3 pounds. An energy source (thermal, mechanical, chemical, or nuclear) will be required to effect the TCVD activation energy requirements.

Pure iron deposits from any of the organometallic TCVD plating compounds will be contaminated to an undesireable degree with codeposited carbon, usually at least 0.7 percent by weight. Such Fe-C deposits display an extreme hardness that is unsuitable for coating thicknesses exceeding a few mils and tend to spall and exfoliate unless extensively heat-treated to remove the carbon. The extreme brittleness of these pure iron TCVD deposits generally make them unsuitable for meeting structural joint objectives (Figure 1).

Pure nickel deposits from any of the organometallic TCVD plating compounds will also be contaminated to an undesireable degree with codeposited carbon. However, unlike iron, carbon does not affect the mechanical properties of the deposit. Such Ni-C deposits are usually soft, ductile, impact-tough but low strength, also unsuitable for meeting structural joint objectives.

Pure aluminum deposits from any of the organometallic TCVD plating compounds will also be contaminated to an undesireable degree with co-deposited carbon. However, similar to nickel, the carbon does not appear to affect the mechanical properties of the deposit. Also, similar to nickel, the deposit is too low strength to be suitable for meeting structural joint objectives.

A TCVD hardening mechanism is clearly needed. As previously discussed in the section I, a TCVD organometallic plating compound, whose deposit is soft, is selected. Also selected is another TCVD organometallic whose deposit will alloy with the first and harden it through solid solution hardening, dispersion hardening, interstitial hardening, etc. The TCVD Ni-Fe-C alloys are examples of this type of development. A virtually infinite variety of alloy compositions are possible but generally one that displays a proper balance between strength and impact toughness is suitable for meeting the structural joint objectives.

The chief limiting factor in making a TCVD structural joint is the tendency for voids and microcracks to be deposited within the weldment. Vee-Type bevels, with radiused edges, greatly enhance the probability of a successful structural joint. A much better TCVD joint is possible if the joint can be "tacked" together with an initial TCVD soft nickel deposit and then sealing the microcrack by peening, filing, etc. The final TCVD should be the high strength, impact-tough composition of the TCVD Ni-Fe-C alloys to be suitable for the structural joint.

The TCVD depositions of Ni/NiO_2 did not appear to materialize as suggested in the literature by Owens (Reference 5). The NiO_2 was, hopefully, to act as a dispersion-hardening mechanism for the otherwise soft TCVD nickel. Possibly the 800°F deposition temperature was too high. Nickel, particularly in the vapor phase deposition, may dissolve a large amount of oxygen, perhaps interstitially, without forming the NiO_2 as a dispersion. Future TCVD temperatures should be of the order of 400 to 500°F.

Martin Company's approach in these researches has been one of simplicity and practicallity. Low temperature TCVD organometallic plating compounds were chosen to provide depositions in a temperature range that does not affect the mechanical or heat treatment properties of the substrate metal. The equipment consists basically of a copper plating chamber and copper tubing process lines. Conventional flowmeters were installed to meter the flow of the organometallics. Palladium catalyst and moisture dessicants were used to purify purging and reducing gases. Mechanical vacuum pumps were used to evacuate the plating system. Cold traps were used ahead of the pump to remove undecomposed, waste organometallics. A high temperature burner was installed and the waste organometallics burned, thereby reducing their toxicity. High vacuum, bellows-type valves were used throughout the plating system.

Conventional, standard electroplating shop procedures were used in the preparations of the various metal substrates. As described more completely in section I metals such as aluminum, titanium, beryllium, and chromium are extremely reactive with oxygen. Conventionally cleaned and activated

metals of the above types, form new oxides (repassivate) films in the time period required to transfer them to the plating chamber and to evaluate the chamber to operating pressures of 10^{-4} torr. Hydrogen reduction of these refractory metal oxides, such as alumina, titania, beryllia, and chromium oxides (stainless steels) require extremely high temperatures and extremely dry hydrogen atmospheres to effect metal oxide reduction (Figure 6). The high temperature approach is counter to the TCVD joint objectives. A more practical approach involves the selection of another metal; one that does not form a refractory metal oxide, such as nickel, copper, tin, iron (see Figure 6). Substrate metals are then cleared free from both organic and inorganic (metal oxide) contaminants and then immediately coated with the selected other metal that does not form refractory oxides using conventional immersion coatings of zinc or tin for aluminum, and electroplated nickel for stainless steels. Oxide films forming on such metal protected substrates are comparatively easily thermally reduced with hydrogen, at acceptably low temperatures. Subsequent TCVD deposits then come into intimate contact with substrate metal atoms without encountering an undesireable, interposing metal oxide interface.

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IV. CONCLUSIONS AND RECOMMENDATIONS

High quality TCVD alloys of Ni-Fe-C have been developed with a range of mechanical properties from the dead soft, pure, ductile nickel to the extremely hard, brittle iron-carbon deposits. Nickel-iron-carbon alloys displaying a Rockwell C hardness from 30 to 52 appear to be the best suited for fabrication of structural joints requiring strength and impact-toughness.

Typical TCVD Ni-Fe-C alloy joints are capable of tensile strengths exceeding 100,000 psi as compared to 40,000 psi for present joints. Tensile failures are at the interface between the substrate and the TCVD deposit, not within the Ni-Fe-C deposit. The current plating system is inadequate in controlling oxygen contamination because both bare and electroplated nickel pretreated stainless steel substrates tend to oxidize during the initial degassing treatment, thereby adversely affecting the subsequent metallurgical bond between the TCVD deposit and the substrate. A diffusion pump capable of evacuating the plating system to at least 10^{-6} torr should be used for all subsequent developments.

The organometallics compounds appear to be excellent sources for low thermochemical vapor depositions of metals. Carbon of varying amounts is invariably codeposited with the metal. Codeposited carbon will affect the physical and mechanical properties of the TCVD deposit, e.g., hardness, corrosion resistance, electrical characteristics, strength, etc. With respect to TCVD joining objectives, codeposited carbon can be used as a TCVD deposit hardening mechanism providing both strength and impact-toughness.

Thermochemical vapor depositions using the organometallic compounds invariably result in the evolution of a large amount of byproduct gas. Gas evolution hinders and impedes the flow of fresh organometallics to the substrate surface, reducing the chemical reaction TCVD kinetics. More importantly the "gushing out" action of these gas molecules from microcracks and holes, as well as joint gaps, greatly restrict the microthrowing power of the TCVD process. Holes, cracks, and other substrate defects initiate these same type defects into and throughout the entire TCVD deposit. Joints tend to remain unjoined and the joint gap remains as a microgap. Microthrowing power, however, can be improved and joint weldments can be made by following newly developed techniques with substrate joint geometries, laminar non-turbulent organmetallic vapor flows, and improved heating methods as discussed in section I.

Metal substrates (aluminum, titanium, chromium, and beryllium) displaying a great affinity for oxygen present a difficult challenge. Metal oxides films must be absent at the time of TCVD in order to effect a metallurgical bond of the deposit to the metal substrate. Typically the above metals form refractory metal oxides. Thermal-hydrogen reduction of such oxides require the substrate to be exposed to temperatures exceeding the recrystallization and often the melting point. Chemically activating substrate metals to remove the surface metal oxides, followed immediately by the application of a suitable metallic, protective film (zincate) for aluminum and nickel electroplate for stainless steels, provides a surface with a far less refractory metal oxide. Low temperature, hydrogen-reductions, are then readily achieveable (Figure 6). Subsequent TCVD are accomplished on metal-oxide free interfaces thereby assuring metallurgical bonding.

Although the TCVD deposition yields are usually high, 70 percent or more (i.e., more than 70 percent of the organometallic yields metal depositions with 30 percent unused and lost) and deposition rates to 100 mils (0.100 inch) per hour, times required to fabricate a joint are long compared to fusion-type welding methods.

TCVD techniques provide a unique mechanism for composite structures. By using several compatible organometallic plating compounds, deposition structures can be grown atom by atom into various homogeneous or hetrogeneous microstructures composites, capable of meeting a wide range of engineering requirements. An elementary example of this technique would be the TCVD Ni-Fe-C alloys. Physical and mechanical properties varying from extremely hard, but brittle (intrinsic strengths greater than 100,000 psi) to extremely soft, but impact-tough (intrinsic strengths of order of several thousand psi) are all possible within one, single composite structure. While other joining methods such as electroplating, electroforming, and physical (vacuum) deposition, might be used for low temperature joining, only the TCVD method offers true versatility for forming elemental or alloy composite microstructures capable of meeting a wide range of engineering service requirements.

Complete control over the TCVD mechanism will permit its application to a number of joining problem areas:

1 Joining of foamed metals, thin foils, and wires to themselves and to other materials

2 Joining metallic to non-metallic materials

3 Joining non-metallic materials to themselves and to other non-metallic materials

4 Joining of members of small cross-sectional area to those of large cross-sectional area

5 Joining of fiber-reinforced composite materials

6 Joining of coated materials.

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APPENDIX A

PHASE IV ALUMINUM ALLOY 2219-T87

SUMMARY

A program directed toward the welding of the aluminum alloy 2219-T87 below its recrystallization temperature was conducted using thermochemical vapor deposition techniques. This feasibility study resulted in the development of techniques for the deposition of aluminum on aluminum, on steel and on copper. The techniques are based on the thermochemical decomposition of tri-isobutyl aluminum in the temperature range of 400 to 500°F. The room temperature properties of the aluminum alloy 2219-T87 are not significantly affected when held in this temperature range for periods up to 1 hour. Although actual weldments were not achieved, the chemical, and metallurgical quality of the deposited metal and its interfacial bond with the substrate was sufficiently high to warrant further development of the process.

This process, when fully developed, should find application in the repair and fabrication of orbiting space platforms, and space vehicles as well as in situations where conventional welding temperatures cannot be tolerated.

PURPOSE

Phase I, part of a three phase NASA sponsored program to determine the feasibility of joining metals by use of thermochemical vapor deposition reactions, concerns the joining of the aluminum alloy 2219-T87.

SCOPE

Phase I concerns the development of procedures for the deposition of elemental aluminum resulting from the thermochemical decomposition of suitable aluminum compounds; and having achieved satisfactory deposition, make and evaluate simple welds.

I. TECHNICAL APPROACH

Initially a survey was conducted to determine those compounds having potential for depositing aluminum below the recrystallization temperature of structural aluminum alloys. A reason for this criterion, as shown in Table I, is that the room temperature mechanical properties of the aluminum alloy 2219-T87 selected for this study are not significantly affected by extended heating at temperatures up to 500°F. The physical and chemical properties of the 2219 aluminum are described in Tables II and III.

TABLE I

Typical Room Temperature Tensile Properties of the Aluminum Alloy 2219-T87 After Holding at Given Temperatures

Temperature °F	Time at Temperature (hr)	Ftu* (ksi)	Fty* (ksi)	Elongation Percent in 2 Inches
75	-	70	58	10
212	1/2	70	58	10
	10	71	58	10
	100	72	59	10
	1,000	72	60	10
300	1/2	70	58	10
	10	70	58	10
	100	70	57	10
	1,000	66	52	10
400	1/2	69	56	10
	10	65	50	10
	100	60	45	11
	1,000	56	41	11
500	1/2	62	46	12
	10	55	39	12
	100	53	37	12
	1,000	51	35	12
550	1/2	57	40	13
	10	53	36	13
	100	48	33	13
	1,000	38	28	14

*Ftu and Fty are respectively the ultimate tensile and yield strengths.

Data Source: ALCOA, New Kensington, Pennsylvania.

TABLE II

Chemical Composition of
Aluminum Alloy 2219

Element	Compositional Range (%)*
Copper	5.8 - 6.8
Manganese	0.20 - 0.40
Zirconium	0.10 - 0.25
Vanadium	0.05 - 0.15
Titanium	0.02 - 0.10
Silicon	0.20
Iron	0.30
Zinc	0.10
Magnesium	0.02
Others, Each	0.05
Others, Total	0.15
Aluminum	Remainder

*Maximum unless shown as a range.

Data Source: ALCOA, New Kensington, Pennsylvania.

TABLE III

Physical Properties of Aluminum Alloy 2219

Specific Gravity	2.83
Density, $lb/in.^3$	0.102
Melting Range, °F	1010 - 1190
Electrical Conductivity at 20°C, Percent IACS	
-0 Temper	44
-T6, -T81, -T87 Tempers	32
-T31, -T37 Tempers	28
Thermal Conductivity at 25°C, CGS Units	
-0 Temper	0.41
-T6, -T81, -T87 Tempers	0.30
-T31, -T37 Tempers	0.27

TABLE III (Cont)

Average Coefficient of Thermal Expansion (-0 Temper), °F x 10^6	
68-212°F	12.4
68-392°F	13.1
68-572°F	13.6

The above values apply equally well to the filler alloy 2319.

Data Source: ALCOA, New Kensington, Pennsylvania.

Joining this alloy at or below the 500°F temperature permits retention of its original structural integrity and precludes the necessity for reheat treatment. Literature searches and contacts with researchers knowledgeable in the pertinent disciplines made it apparent that the organometallics held the most promise for the deposition of aluminum in the desired temperature range. Following these surveys three candidate materials were selected (References 1 through 9):

1 Aluminum acetylacetonate

2 Tri-methyl aluminum (TMA)

3 Tri-isobutyl aluminum (TIBA)

On further theoretical examination it was found that each candidate material had limitations. With aluminum acetylacetonate, the internuclear bond distance for the Al-O is shorter than that for its C-O bond; therefore, less energy is required to cleave the C-O bond; hence, it fractures with heating prior to deposition of aluminum. Depositing aluminum from this compound requires temperatures in excess of 850°F which results in low quality carbonaceous deposits.

The aluminum alkyls, such as tri-methyl aluminum and tri-isobutyl aluminum, are very stable at room temperature; however, at elevated temperatures they decompose by several mechanisms. In the temperature range of 390 to 480°F they decompose into the dialkyl hybride and olefin (References 4, 7, and 8):

$$(RCH_2CH_2)_3Al \longrightarrow (RCH_2CH_2)_2AlH + RCHCH_2$$

By increasing the temperature further (References 8 and 9) complete decomposition results in the formation of aluminum metal, hydrogen, hydrocarbon mixtures and aluminum carbide. Tri-methyl aluminum which exists as a stable dimer in the vapor state requires relatively high temperatures for its dissociation which causes powdery deposits of aluminum carbide (Reference 9). Tri-isobutyl aluminum, on the other hand, exists as a monomeric beta-branching molecule which decomposes with relative ease. In the presence of oxygen the aluminum alkyls form alkoxides readily (References 4, 5, and 6):

$$2\ R_3Al + 3\ O_2 \longrightarrow 2\ (RO)_3Al.$$

These alkoxides form alcohols on subsequent hydrolysis.

Tri-isobutyl aluminum was selected as the most promising material for the thermochemical vapor deposition of aluminum on aluminum (References 10, 11, 12, and 15). Table IV presents physical characteristics of the organometallic compound.

NOTE

Aluminum alkyls react readily with air or oxygen. The members with alkyl groups smaller than butyl spontaneously ignite upon contact with air (References 1 and 6). Oxidation under controlled conditions produces the alkoxides in high yield:

$$2\ R_3Al + 3\ O_2 \longrightarrow 2\ (RO)_3Al$$

The oxidation has been postulated to proceed via peroxides (Reference 2). Subsequent hydrolysis of the alkoxides produces alcohols. Sulfur and selenium react similarly to oxygen except that the reaction is not so vigorous (Reference 13). Mercaptans are obtained on hydrolysis.

The thermal decomposition of tri-isobutyl aluminum in the temperature range of 430 to 500°F proceeds as follows:

$$(C_4H_9)_3Al + C_4H_8 \longrightarrow Al + 1.5\ H_2 + 4\ C_4H_8.$$

Since this material is pyrophoric and reacts violently with water, both air and moisture must be excluded from the reaction. Therefore, it was

decided to conduct the experiments at low vacuum using dry carrier gases such as argon and nitrogen.

TABLE IV

Physical Properties of Tri-Isobutyl Aluminum

Formula	$(i\text{-}C_4H_9)_3Al$
Formula Weight	198.328
Composition, Weight	
Tri-isobutyl Aluminum (based on soluble aluminum corrected for aluminum hydride content)	95.6 min
Aluminum Hydride Equivalent (probably present as di-isobutyl aluminum hydride)	0.5 max
Tri-n-butyl Aluminum	nil
Dissolved Isobuylene	2.5 max
Soluble Aluminum	13.4 min
State and Color at 25°C (77°F)	Clear Colorless Liquid
Stability in Contact:	
Air	Fumes Violently
Water	Reacts Violently
Freezing Point	1.0°C (33.8°F)
Boiling Point at 30 mm Hg	113.8°C (236.8°F)
Vapor Pressure, mm Hg:	
50°C (122°F)	0.95
90°C (194°F)	9.9
130°C (266°F)	58.0
Density at 20°C (68°F)	
g/ml	0.7876
lb/gal	6.573
Viscosity at 20°C (68°F), cp	2.301

The apparatus developed for and during the experimentation of Phase I consisted of a reaction chamber, reactant supply bottles, a vaporizing-mixing chamber, carrier gas source, suitable metering devices, control and indicating devices, filters and purifiers, hydrocarbon and cold traps, a vacuum pump, a 10 kw induction heater and coil, and suitable conduit. Figures 1 through 5, present a schematic and photographs of the equipment.

Initial experimentation concerned calibration of the induction equipment and the design of induction coils to provide localized heating of the aluminum specimen. These experiments were conducted in an argon atmosphere at a vacuum of 300 mm of mercury. Considerable arcing and corona effects were experienced. The experiments were conducted in nitrogen under the same vacuum; arcing and corona were less noticeable, but still present. Reducing the vacuum to 100 mm Hg gave only sporadic relief. Finally, steel substrate heater plates were used to reduce the power requirement; this solved the problem. Figure 5 shows the heater plate, specimen and induction coil arrangement used for all deposition experiments.

To assist in visually determining that deposition of aluminum was occurring, copper specimens were used in the early experimentation. To assist in determining deposition temperatures, steel substrates were used because of ease of cleaning and control of heating. For deposition on aluminum both the aluminum alloy 1100 and 2219-T87 were used. The materials and cleaning procedures used are described in Tables V and VI.

TABLE V

Materials Used During TCVD Experimentation

Material	Application	Description
Nitrogen	Carrier Gas	Extra dry, dew point -93°F (4 ppm) Source: Amercian Cryogenics
Argon	Carrier Gas	Purity, 99.999 percent, dew point -76°F Source: American Cyrogenics
Isobutylene	Reactant	Research Grade (99.26 percent) and Chemically Pure (99.0 percent min) Source: The Matheson Company
Tri-isobutyl Aluminum	Reactant	Purity, 95.6 percent min Source: Ethyl Corporation

TABLE V (Cont)

Material	Application	Description
Aluminum	Substrate	Aluminum Alloy 2219-T87 Aluminum Alloy 1100 Annealed Source: Aluminum Corporation of America
Copper	Substrate	QQ-C-576, Cold-rolled, soft annealed
Steel	Substrate	AISI 1020 Source: U.S. Steel
Steel	Heater Plate	Stainless Steel, Type 321 MIL-S-6721A Source: Allegheny Ludlum

TABLE VI

Experimental Cleaning Procedures Used

Procedure 1.
- Step a. Solvent clean (benzene)
- b. Alkaline clean (hot)
- c. Pickle (nitric acid)
- d. Distilled water rinses were used between each of the above
- e. Forced gas drying (argon).

Procedure 2.
- Step a. Solvent clean (benzene)
- b. Alkaline clean (hot)
- c. Neutralization (dilute HCl)
- d. Distilled water rinses between each of the above steps
- e. Forced gas drying (argon)
- f. Hone (silicon carbide No. 90 grit)
- g. Clean (argon blast)
- h. Abrasive paper abrade immediately before deposition
- i. Clean (argon blast).

Note: Aluminum specimens were cleaned according to Procedure 2.
Copper specimens were cleaned using either of the above.
Steel specimens were cleaned according to Procedure 2.

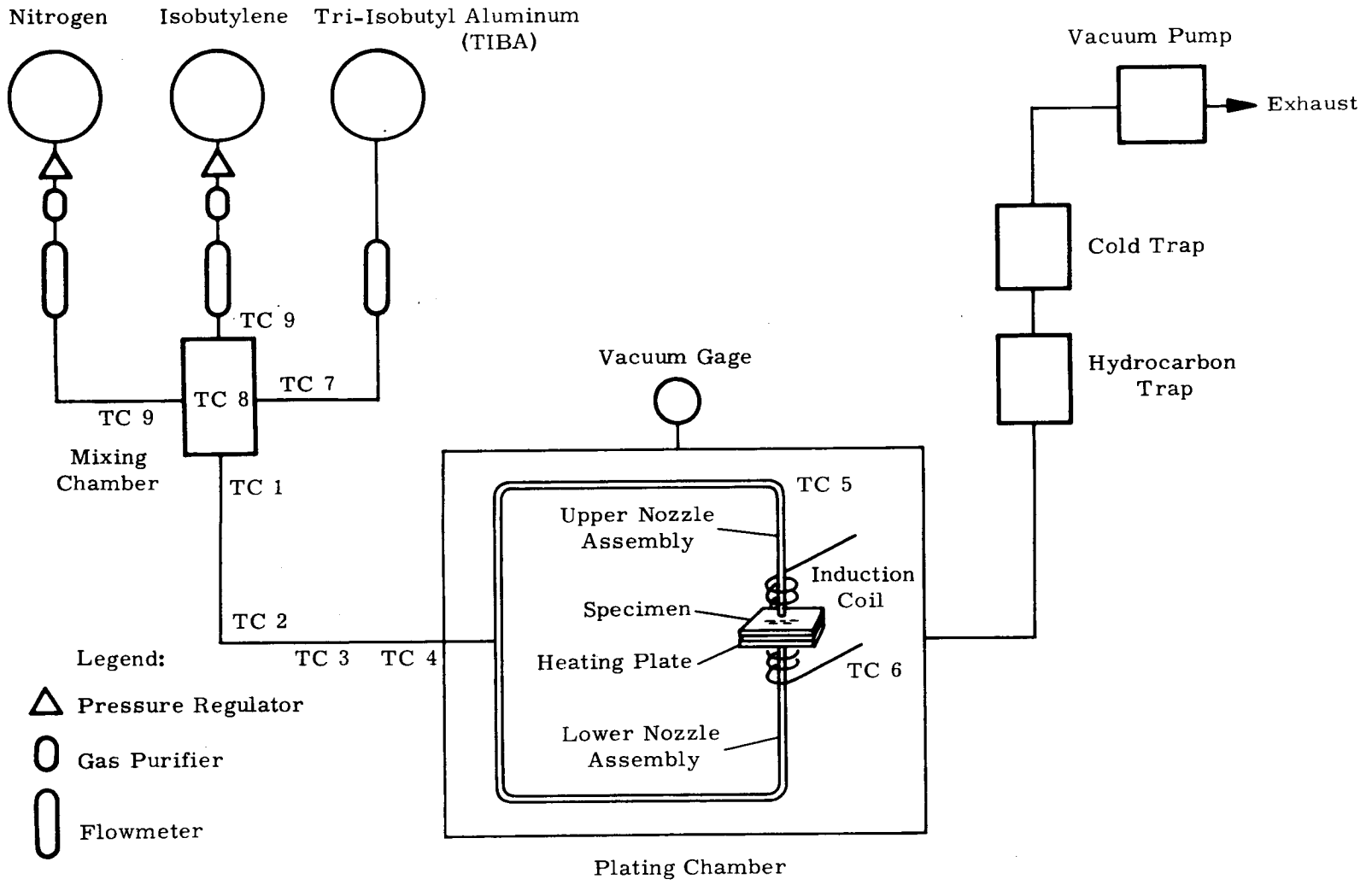

Figure 1. Schematic for Thermochemical Deposition of Aluminum

Figure 2. Apparatus Used for Thermochemical Vapor Deposition

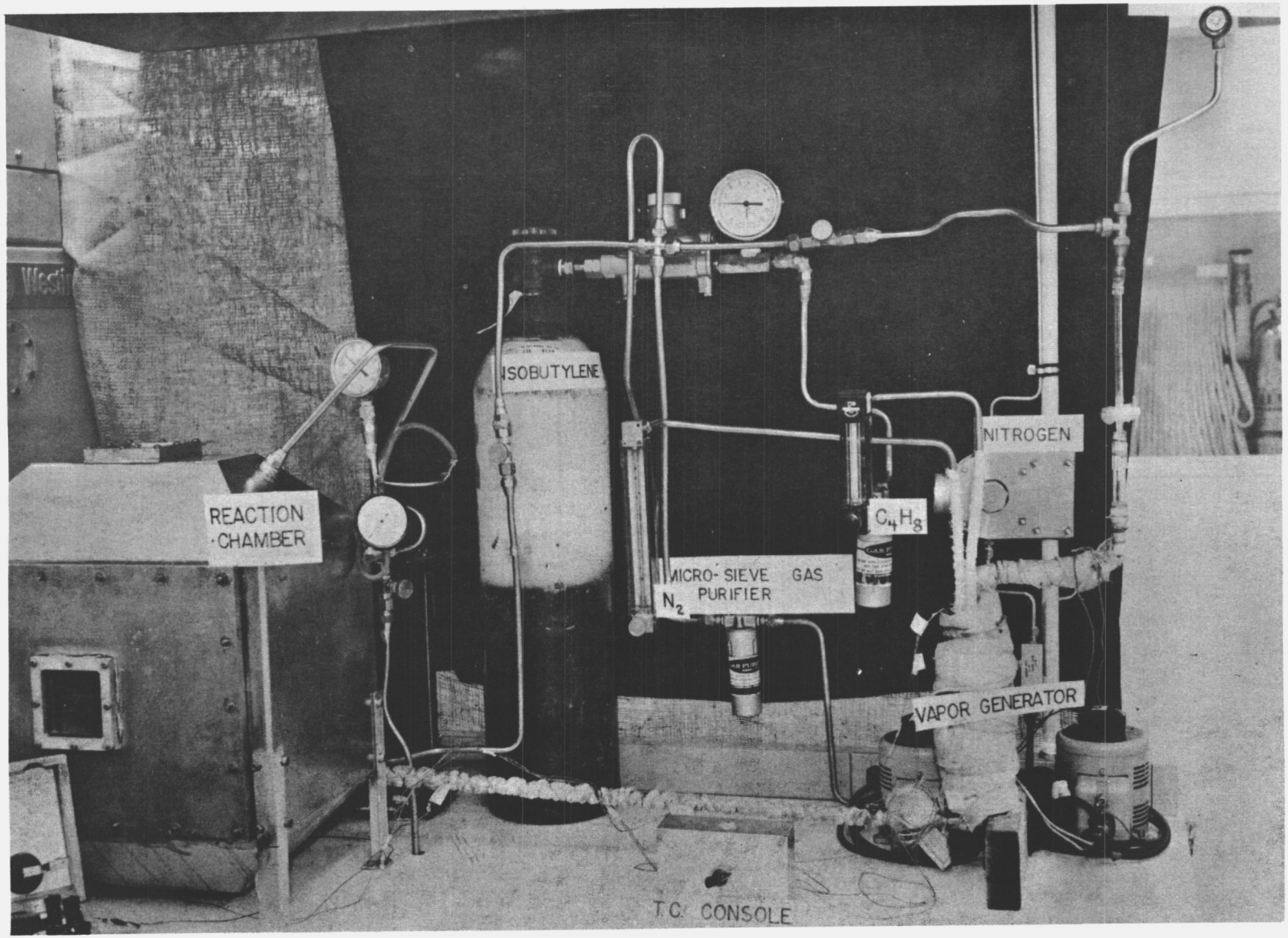

Figure 3. Closeup of Thermochemical Vapor Deposition Apparatus

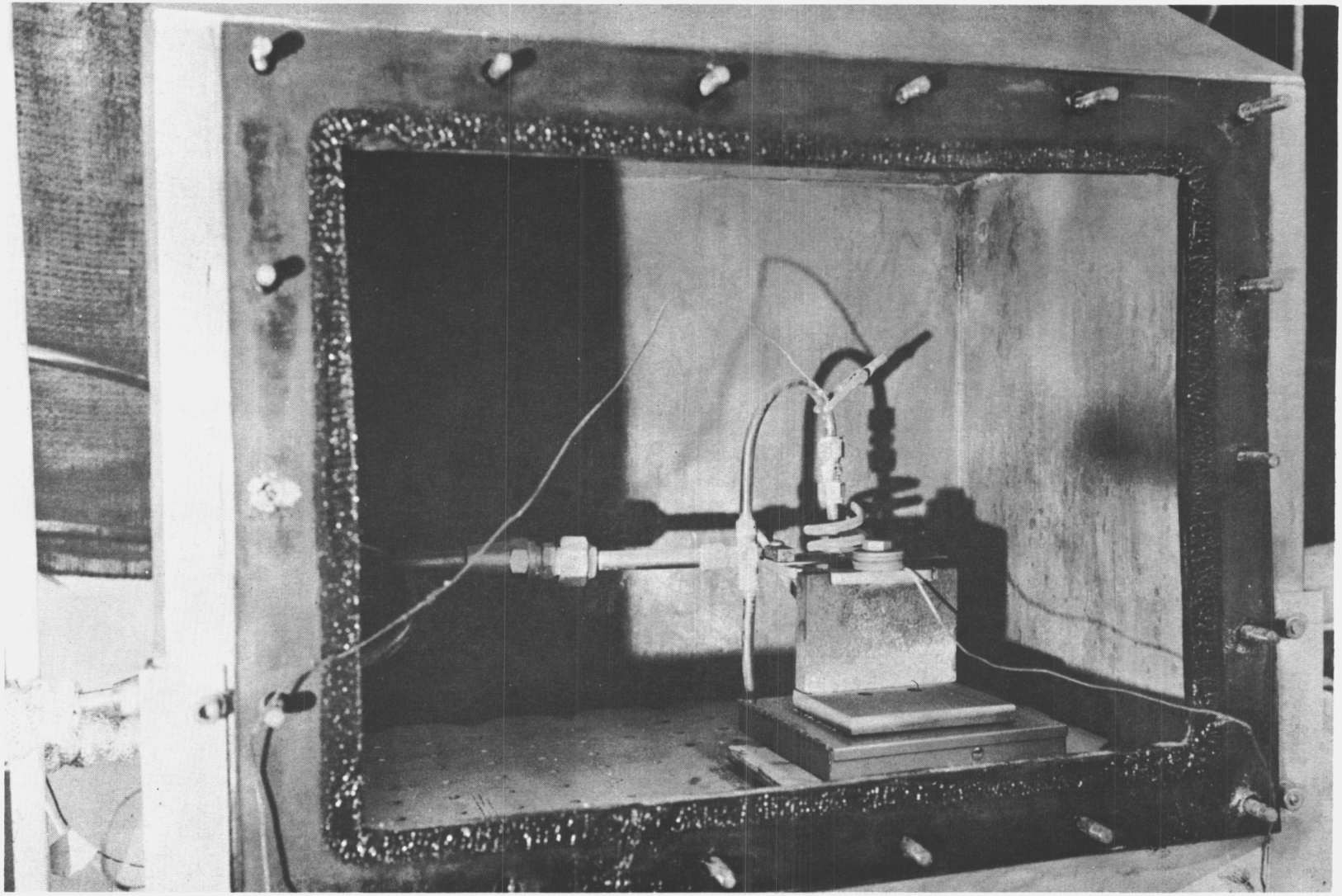

Figure 4. Interior of Deposition Chamber Showing Specimen Holder, Induction Coils and Nozzle Assembly

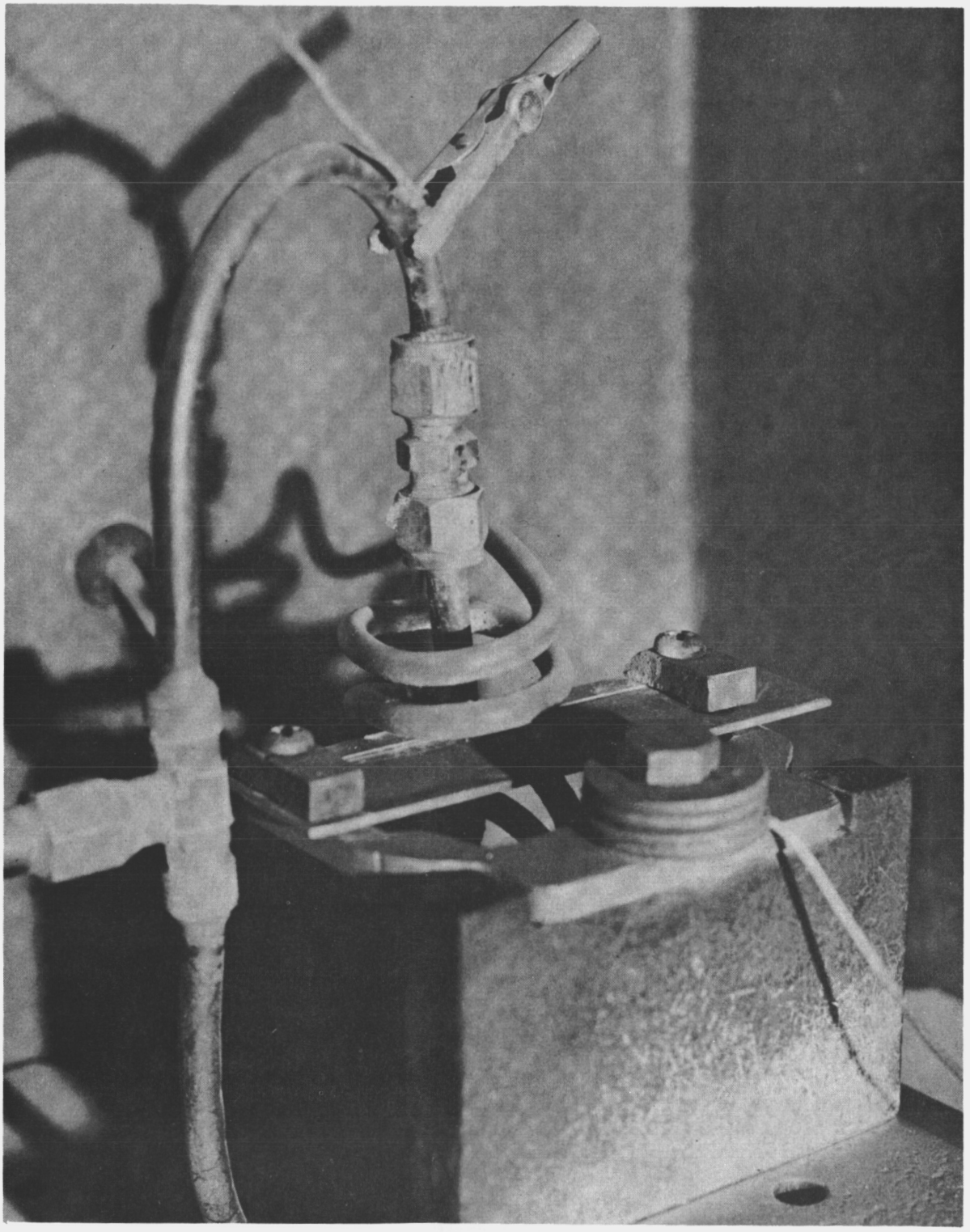

Figure 5. Closeup of Specimen Holder, Aluminum Specimen on Steel Heater Plate and Induction Coils and Nozzles

In making a deposit, the specimen is positioned on the heater plate substrate which in turn is located between the reactant nozzles and the induction coils. Prior to heating the specimen, the reaction is purged at least three times with high purity extra dry nitrogen (dew point, -93°F) by cycling the chamber pressure between atmospheric pressure and a vacuum of 760 mm Hg. During the purging operation, the temperature of the vaporizer is brought to about 310°F; the mixing chamber and conduit to the reaction chamber is stabilized at about 375°F. The nitrogen and isobutylene flow is adjusted with the system thermally stabilized. The chamber pressure is then adjusted to 100 mm Hg vacuum. The specimen is brought to 500°F by energizing the induction coil. When its temperature is stabilized, the triisobutyl aluminum is metered at about 0.8 milliliter per minute into the vaporizer. The TIBA vapors proceed to the mixing chamber where they are mixed with the carrier gas and isobutylene. The isobutylene is added at the rate of one stoichiometric volume to prevent the formation of the diisobutyl aluminum hydride which early experimentation showed to inhibit the rate of aluminum deposition by tying up the available aluminum:

$$(C_4H_9)_3Al \xrightarrow{250°F} (C_4H_8)_2AlH + C_4H_8.$$

By adding the isobutylene, the reaction proceeds theoretically as follows:

$$(C_4H_9)_3Al + C_4H_8 \xrightarrow{500°F} Al + 1.5\ H_2 + 4\ C_4H_8.$$

At the conclusion of the deposition reaction, the chamber is carefully purged and the specimen is removed for evaluation.

During deposition, the reaction chamber effluents are conducted through a cold trap and a kerosene trap to prevent unspent reactants from coming in contact with the atmosphere where they would react violently.

The specimens were subsequently evaluated visually, physically, metallographically and chemically to determine the general appearance, the rate of deposition, the nature of the deposit, the integrity of the bond interface and the effects on the substrate metal. Mechanical properties were not obtained, because the slow deposition rates precluded actual weldments.

The actual experimental procedures are outlined in the Appendix.

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II. RESULTS

The research conducted indicates a definite feasibility for the joining of the aluminum alloy 2219-T87 by thermochemical vapor deposition involving tri-isobutyl aluminum. High purity aluminum deposits on aluminum were achieved at rates up to 15 mils per hour in the temperaure range of 420 to 500°F, the latter appearing optimum. Above 520°F, the deposits become nodular, puffy and carbonaceous because of the premature chemical breakdown of the TIBA and the formation of carbides. Tolerance of the process to oxygen and moisture is below 30 ppm, necessitating the use of high purity carrier gases and reactants. Excess oxygen causes the formation of aluminum oxide, while excess moisture causes premature breakdown of the TIBA.

While actual weldments were not made, mainly because of the slow deposition rates achieved, the excellent chemical and metallurgical quality of the deposited metal and its interfacial bond with the substrate supports the premise that welding is possible by this method.

Table VII presents the results of the experiments conducted during this phase of the research. Figures 6 through 11, present photomicrographs showing the quality of the deposited aluminum and its interfacial bond with its substrate.

The efficiency of the process based on the aluminum available in the tri-isobutyl aluminum is approximately 4 percent.

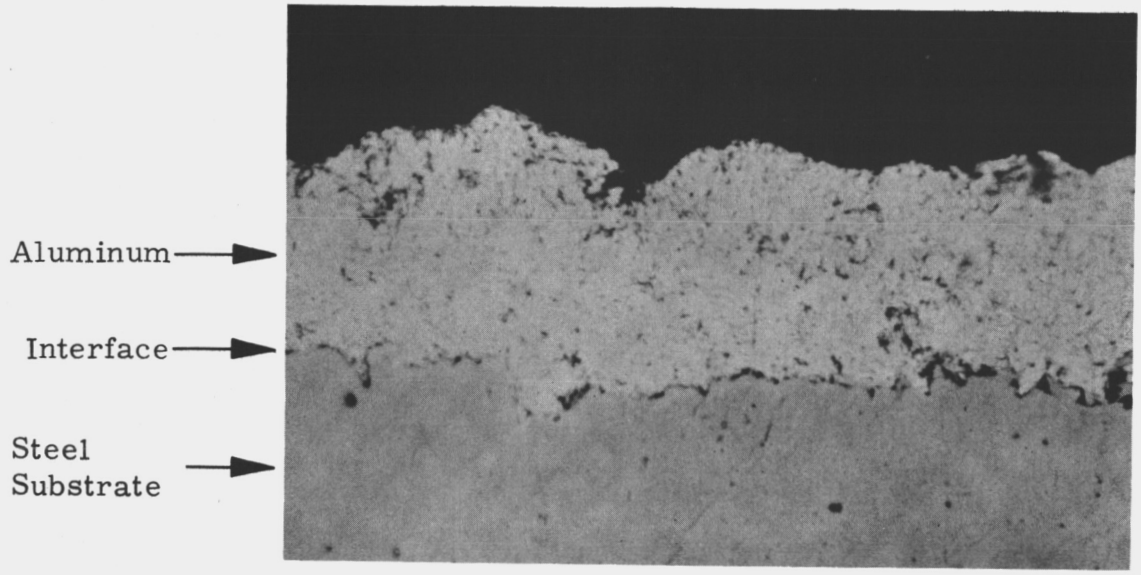

Figure 6. Photomicrograph of Thermochemically Vapor Deposited Aluminum on Steel; Magnification 1500X; Unetched

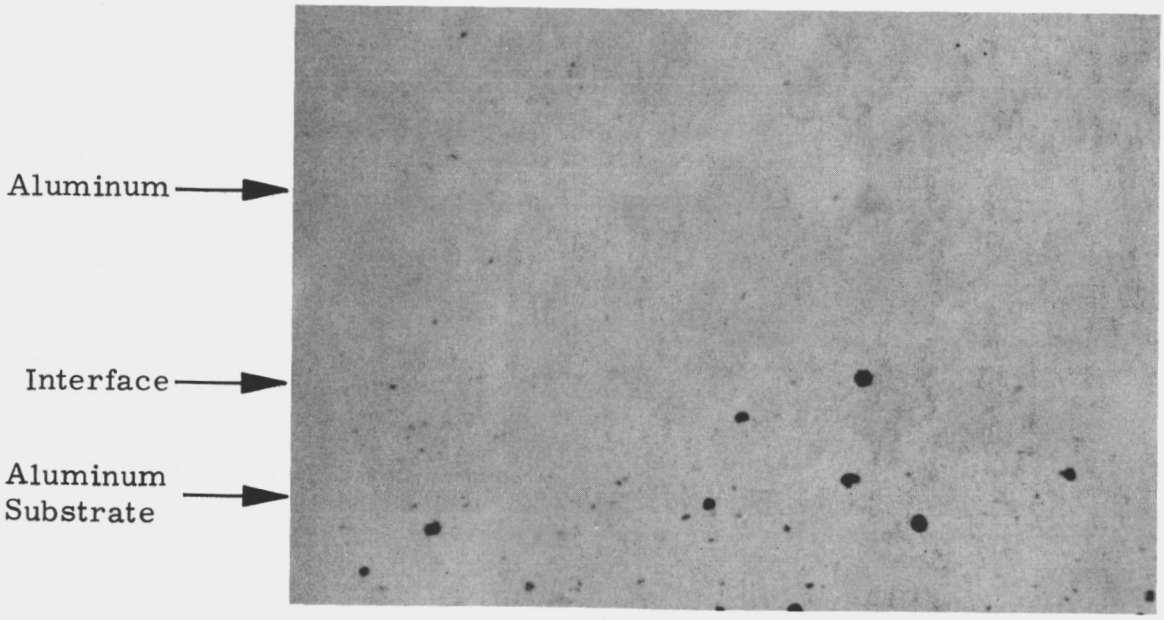

Figure 7. Photomicrograph of Thermochemically Vapor Deposited Aluminum on an Aluminum Alloy (2219-T87) Substrate; Magnification 500X; Unetched

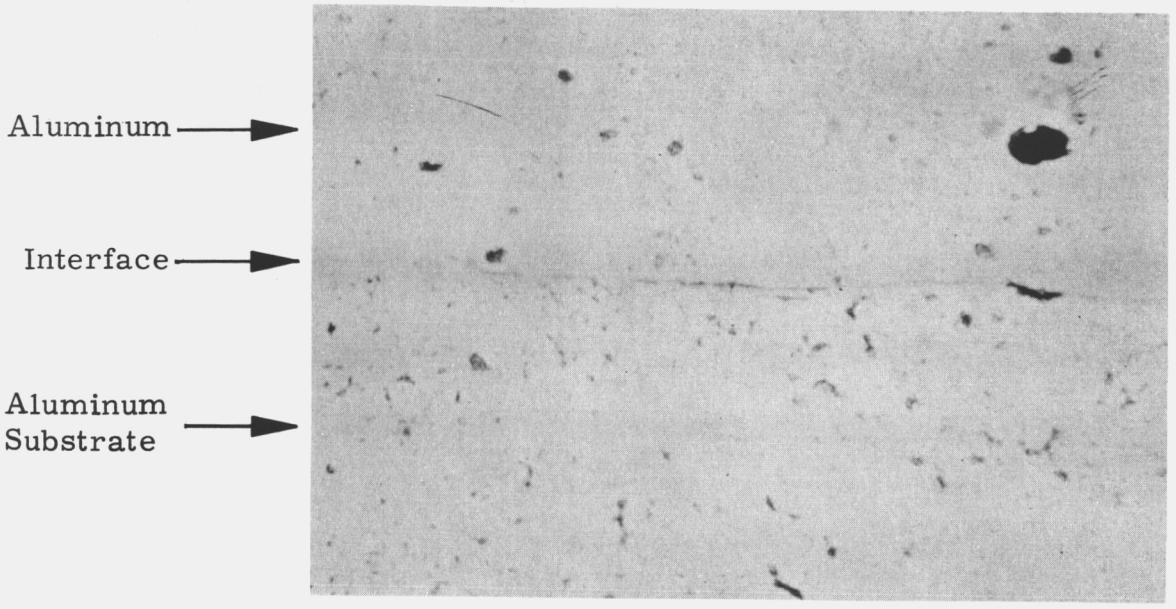

Figure 8. Photomicrograph of Thermochemically Vapor Deposited Aluminum on an Aluminum Alloy (2219-T87) Substrate; Magnification 1500X; Unetched

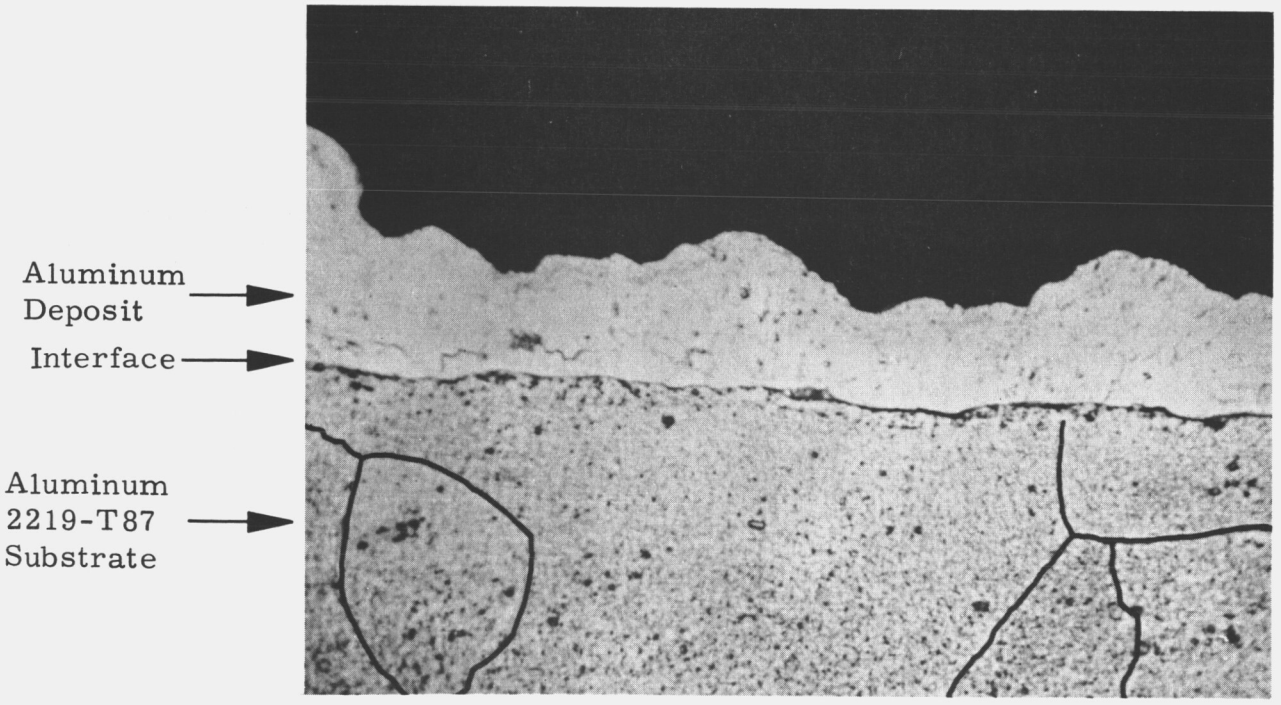

Figure 9. Photomicrograph of Thermochemically Vapor Deposited Aluminum on an Aluminum Alloy (2219-T87) Substrate; Magnification 1500X; Etchant - Kellers

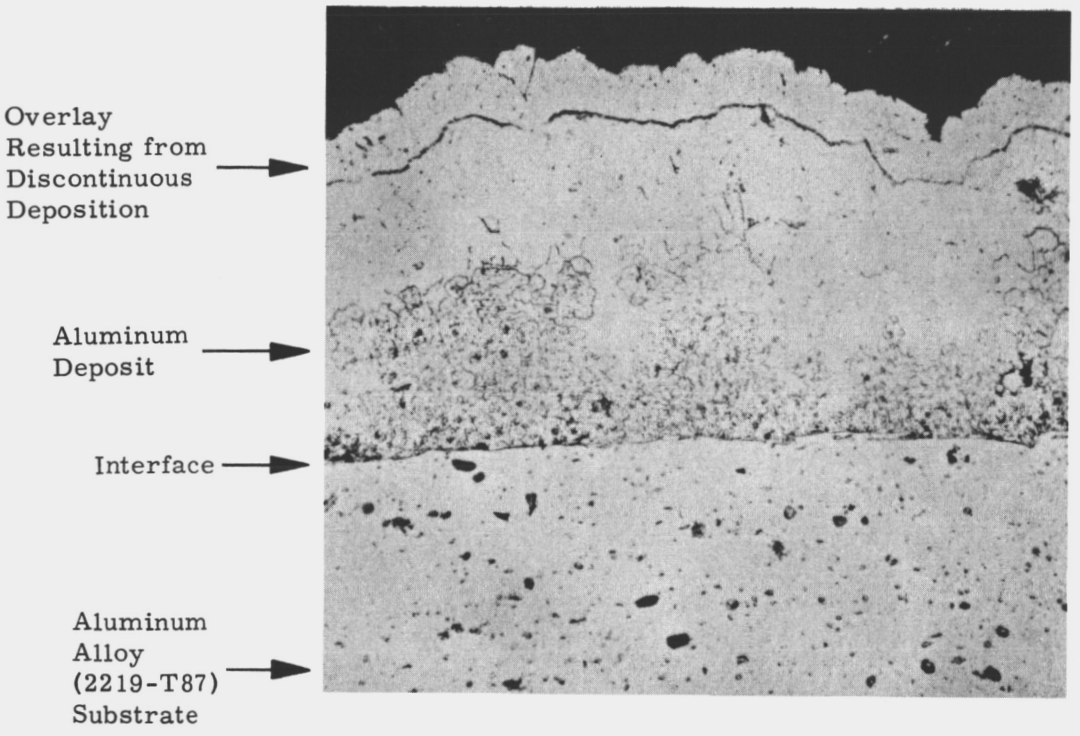

Figure 10. Photomicrograph of Thermochemically Vapor Deposited Aluminum on Aluminum (1100) Substrate; Magnification 500X; Etchant - Kellers

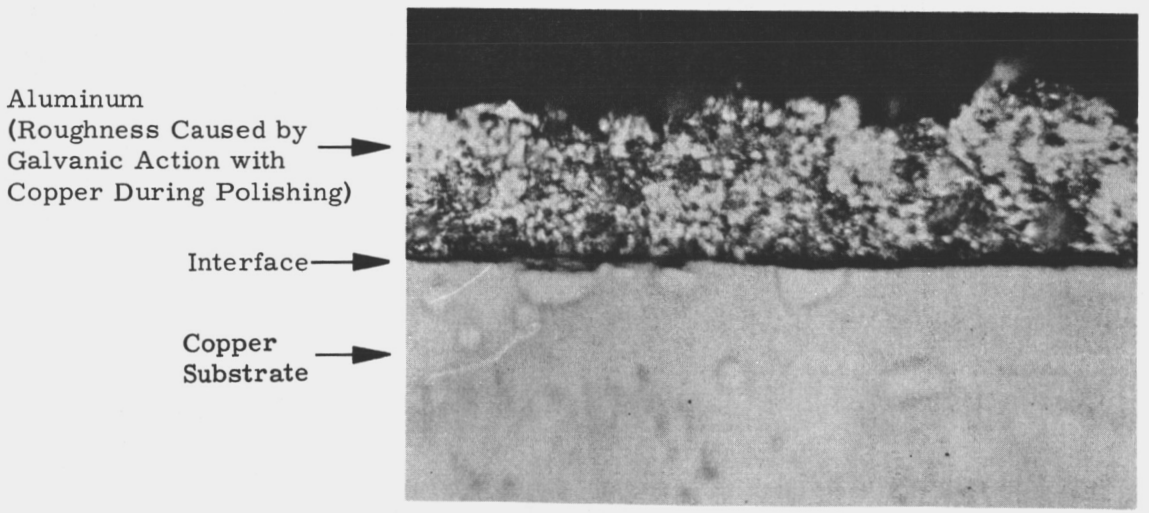

Figure 11. Photomicrograph of Thermochemically Vapor Deposited Aluminum on Copper; Magnification 1500X; Unetched

TABLE VII

Thermochemical Vapor Deposition (TCVD) of Aluminum From Tri-Isobutyl Aluminum

Run No.	Objective	Process Parameters*	Appearance of Plate	Comments
1	Process and system checkout	Substrate - pure copper, QQ-C-576 cold-rolled, soft-annealed, 0.030 by 1 by 2.5 inch, preparation - cleaning procedure No. 1 Heating Method - 10 kw dual frequency RF generator; inductively heated steel base plate Nozzle Material - copper, WW-I-799, size 1/8 inch OD tubing, 0.03 by 0.25 orifice, 1/4 inch distance to specimen, upper and lower nozzle assembly Process Control - pressure 310 mm Hg, flowrates (ml/min) - argon carrier gas 500, reactive gas isobutylene 150, tri-isobutyl aluminum (TIBA) 0.75; temperatures - vaporizing lines 320°F, specimen 490°F; deposition time 90 minutes	Heavy, white, crystalline deposit loosely adherent on copper; probably aluminum oxide	Unsatisfactory deposit caused by oxygen and moisture contamination
2	To study the effect of small amounts of air (100 ppm) present during deposition of aluminum on copper	Substrate, heating method, and nozzle material same as Run No. 1. Process Control - pressure 460 mmHg; flowrates (ml/minute) - argon 750, isobutylene 98, TIBA 0.75; temperatures - vaporizing lines 320°F, specimen 500°F; deposition time 87 minutes	Heavy, white, crystalline deposit similar to Run No. 1	Even small amounts of oxygen/moisture (air) are detrimental to the TCVD reaction
3	Evaluate nitrogen as a carrier gas in an effort to reduce arcing of induction coil during deposition reaction of aluminum on copper	Substrate, heating method, and nozzle material same as Run No. 1. Process Control - pressure 460 mmHg; flowrates (ml/min) - nitrogen 750, isobutylene 110, TIBA 0.42; deposition time 99 minutes	Similar to Run No. 1; dissection of TIBA process line revealed high quality aluminum TCVD deposits	Nitrogen gas (substituted for argon) greatly reduced arc/corona tendency
4	Evaluate effects of faster removal of reaction products on the quality of aluminum deposition on copper	Substrate, heating method, and nozzle material same as Run No. 1. Process Control - pressure 660 mmHg; flowrates (ml/min) - nitrogen 625, isobutylene 265, TIBA 0.42; deposition time 235 minutes	Aluminum/aluminum oxide mixed deposition	Flowrates appear much too high; large amounts of white vapor filling plating chamber (obscuring viewing)
5	Reduce carrier and reactant gas flowrates to effect a fine-grained aluminum deposit on copper	Substrate, heating method, and nozzle material same as Run No. 1. Process Control - pressure 660 mmHg; flowrates (ml/min) - nitrogen 250, isobutylene 38, TIBA 0.42; deposition time 35 minutes	Fine-grain aluminum deposit; some straining	Deposition rates appear slow; stain residues, perhaps due to localized overheating of the specimen, causing a pseudo-carbonaceous deposit
6	Same as Run No. 5 except for increased deposition time and decreased isobutylene flow (catalytic suppressant)	Same as Run No. 5 with deposition time increased to 170 minutes and isobutylene flowrate 25 ml/min	Same as Run No. 5	Same as Run No. 5; TCVD yield very low, i.e., no measureable thickness build-up
7	Same as Run No. 5 except for increased deposition time and increased isobutylene flow	Same as Run No. 5 with deposition time 50 minutes and isobutylene flowrate 150 ml/min	Same as Run No. 5	Isobutylene apparently not strongly influential on the TCVD aluminum yield/rates deposition
8	Aluminum deposition on copper . . . better vaporization of the tri-isobutyl-aluminum (TIBA) through increased heat to TIBA vaporizing lines	Substrate, heating method, and nozzle material same as Run No. 1. Process Control - pressure 660 mmHg; flowrates (ml/min) - nitrogen 125, isobutylene 38, TIBA 0.42; temperature of vaporizing lines increased from 320 to 375°F	Same as Run No. 5	Raw, liquid TIBA occassionally slugging over onto the specimen (unheated nozzle)
9	Same as Run No. 8 except nozzle lines thermally insulated in an attempt to prevent TIBA condensing in the unheated nozzle line	Same as Run No. 8 except nozzle line thermally insulated with a thick coating of baked vinyl (organosolve); deposition time 65 minutes	Same as Run No. 5	Technique unsuccessful, i.e., TIBA still condenses in nozzle lines
10	Same as Run No. 8 except TIBA vaporizing line temperatures further increased (to maximum, i.e., just beginning TCVD)	Same as Run No. 8 except temperature of vaporizing process lines increased to 410°F; deposition time 60 minutes	Same as Run No. 5	Technique still unsatisfactory; i.e., TIBA still condenses in nozzle lines

*For a complete description of the process experiment refer to Martin Company, Orlando, Florida, Engineering Notebook No. 8079 (Ralph Wilson).

TABLE VII (Cont)

Run No.	Objectives	Process Parameters	Appearance of Plate	Comments
11	Same as Run No. 5 except with a nichrome heating element added to nozzle assembly	Same as Run No. 5 except temperature of nozzle line increased from ambient room temperature to 300°F through the addition of a nichrome electric heating element; deposition time 120 minutes	Better appearance aluminum deposition; rate ≈ 9 mils/hr	Successful TIBA vaporization
12	Aluminum deposition on copper . . . re-examination of carrier gas flowrates (improved nozzle vaporizing of TIBA)	Substrate, heating method, and nozzle material same as Run No. 1. Process Control - pressure 660 mmHg; flowrates (ml/min) - nitrogen 125, isobutylene 38, TIBA 0.42; temperatures of vaporizing lines 350°F; deposition time 80 minutes	Same as Run No. 11	Carrier gas flowrates of approximately 125 ml/min maximum, i.e., greater rates give white vapor in chamber, obscuring viewing
13	Aluminum deposition on aluminum (copper substrate may adversely effect yields; thickness build-up)	Substrate aluminum alloy 2219, size 0.060 by 1 by 2.5 inch. Heating method and nozzle configuration same as Run No. 1. Process Control - pressure 660 mmHg, flowrates (ml/min) nitrogen 500, isobutylene 75, TIBA 0.42; temperature of vaporizing lines 320°F; deposition time 90 minutes; cleaning procedure No. 2	Thin aluminum deposit on aluminum substrate; deposition rates ≈ 0.009 in/hr	Aluminum substrate offers no deposition yield (rate) over copper substrates (apparently no substitute catalytic effects)
14	Aluminum deposition on butt weld aluminum substrate	Same as Run No. 13 except for substrate butt weld geometry (0.005 inch weld gap); deposition time 170 minutes; aluminum substrate 3003 alloy	Deposit consists of nodular aluminum, carbonaceous powders, aluminum oxide crystals; no joint	Temporary overheating of specimen from desireable 500°F to over 600°F over decomposed the TIBA TCVD reaction
15	Same as Run No. 14, emphasis on substrate thermal control	Same as Run No. 14; deposition time 135 minutes	Same as Run No. 14 but far less carbonaceous and Al_2O_3 deposits; no joint	Again, momentarily overheating as Run No. 14
16	Same as Run No. 14, emphasis on substrate thermal control	Same as Run No. 14; deposition time 100 minutes	Better aluminum deposit; low yields; no joint	Deposition rate ≈ 0.013 in/hr
17	Aluminum deposition on copper, reduced TIBA flowrates	Substrate, heating method, and nozzle material same as Run No. 1. Process Control - pressure 660 mmHg; flowrates (ml/min) - nitrogen 125, isobutylene 50, TIBA 0.10; deposition time 90 minutes	Good aluminum deposit 0.019 inch thick (90 minute deposition)	
18	Same as Run No. 17, study TCVD mechanism	Same as Run No. 17; deposition time 125 minutes	Good aluminum deposit; deposition rate 0.015 in/hr (highest yield to date)	Several purging prior to TCVD promotes high quality deposits, i.e., reduces plating systems O_2H_2) residuals

III. DISCUSSION

The thermochemical vapor deposition process shows definite promise for "in-space" fabrication and repair of the space structures and orbiting vehicles. In the hard vacuum of outer space many of the problems encountered with the process in the earth atmosphere are non-existent. For example, oxygen and moisture contamination ceases to be a problem; also, in the case of tri-isobutyl aluminum, the vaporizing temperature is reduced to approximately 47°F and, hence, the formation of the troublesome di-isobutyl aluminum hydride is avoided. The formation of this latter compound interferes with the aluminum deposition reaction. Cleanliness of the surfaces to be joined is of small import, since in outer space surfaces tend to be self-cleaning. The weight and bulk of the apparatus required is insignificant; a typical container 2 inches in diameter and 14 inches long weighs only about 3 pounds.

One of the limiting factors in Martin Company's Phase I research has been the inability to increase the rate of deposition. One of the reasons for this may be a catalytic effect of the copper apparatus and lines used in the experimentation. One of the clues to this possibility, is that the deposition rate on copper is initially very high; this rate, however, immediately decreases as the copper specimen becomes coated with aluminum. In addition, although the copper gas-vapor conduit lines are kept below the temperature required for the deposition reaction, these lines were found to be coated with aluminum when subsequently examined. Future work should be conducted in glass apparatus.

Discussion with technical personnel of the Ethyl Corporation, manufacturers of tri-isobutyl aluminum, indicate that deposition rates are nomally in the range experienced in this program, however, the Ethyl Corporation has developed a new organometallic aluminum compound which is claimed to deposit aluminum more rapidly. The compound is presently "company proprietory;" when the compound becomes available, it should be considered for evaluation.

Although the objective of depositing elemental aluminum on aluminum was achieved, the composition of the deposited metal is very pure aluminum, hence the mechanical properties as evidenced by the softness and malleability are quite low. For this reason, future research should include the codeposition of aluminum with alloying elements such as copper, zinc, tantalum and columbiun. Properly dispersed oxides codeposited with the aluminum should also aid in increasing the mechanical properties of the deposited metal.

Martin Company's approach in these researches has been simplicity and practicality. For example, an organometallic compound was chosen which would deposit aluminum in a temperature range which does not adversely affect the mechanical properties of the aluminum alloy 2219-T87. The equipment is quite simple, consisting of standard copper plumbing and a metal reaction chamber. Exotic equipment normally used in vacuum techniques was not used. The reaction pressures used were reasonably close to atmospheric and indicate that the process will operate effectively at atmospheric pressure; hence, it is possible that welding techniques developed for titanium and its alloys might be applicable here. Conventional cleaning procedures were used in the preparation of the substrate metals. While these methods provided surfaces suitable for good adhesion of the deposits, it is felt that additional improvement in the interfacial bond can be achieved by ion-bombardment of the surfaces to be joined immediately before deposition.

IV. CONCLUSIONS AND RECOMMENDATIONS

High quality aluminum deposits on aluminum can be achieved using thermochemical vapor deposition (TCVD) techniques involving tri-isobutyl aluminum. Deposition is achieved in a temperature range (400-500°F) which will not adversely affect the mechanical properties of the aluminum alloy 2219-T87.

Additional development is required to adapt this process to the production of high strength quality welds; therefore, the following studies are recommended preparatory to actual welding:

1. Evaluate the TCVD reaction in a higher vacuum such as 0.2 to 2 torr.

2. Evaluate the TCVD reaction in the absence of copper.

3. Evaluate the Ethyl Corporation's new "proprietary compound" which reportedly will deposit more rapidly than tri-isobutyl aluminum.

4. Perform codeposition studies involving metals and metallic oxides in an effort to enhance the mechanical properties of the deposited metal.

5. Evaluate ion-bombardment techniques as a means of providing chemically clean surfaces just prior to metal deposition.

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APPENDIX B

PHASE IV BERYLLIUM

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I. INTRODUCTION

Beryllium metal is difficult to join both to itself and to other metals. Two basic intrinsic characteristics of beryllium cause difficulty:

1. The metal in the hardened condition most useful for high strength, stiff structures is highly notch sensitive. (Any joining method that produces cracks or microcracks, as fusion welding often does, can severly limit the metal's structural properties.)

2. The metal is extremely chemically reactive toward other metals, forming alloys and intermetallics, and to non-metals, forming brittle ceramic type compounds (oxides, carbides, borides, etc.), again adversely limiting structural properties.

Chemical-vapor deposition (CVD) with its normally lower deposition temperatures is less apt to affect the heat treatment or introduce cracks or microcracks into the beryllium structure. The use of a controlled atmosphere during CVD also reduces contamination in the chemical-vapor deposit. For these reasons a field and literature search has been made to determine the state-of-the-art of beryllium CVD as a feasible method for structurally joining beryllium, particularly to itself.

Beryllium metal offers an unmatched combination of lightweight, stiffness, strength at temperatures up through 1000°F and heat capacity. Offsetting these advantages, are toxicity, brittleness, and high cost both in material and fabrication processes.

II. DISCUSSION

An extensive field survey and literature search was made to determine whether the state-of-the-art for beryllium chemical-vapor deposition has advanced enough to offer a good method for joining beryllium structures.

The following Indexes and Abstracts have been examined for references applicable to beryllium chemical-vapor deposition (CVD):

1. International Aerospace Abstracts

2. American Society For Metals Review of Metal Literature

3 Engineering Indexes

4 Applied Science and Technology Index

5 Selected Listing of NASA Scientific and Technical Reports

6 Technical Abstract Bulletins (TAB)

7 Scientific and Technical Aerospace Reports

8 Chemical Abstracts.

Subject headings: thermal-chemical vapor deposition, vapor deposition, vacuum deposition, gas plating, chemical-vapor deposition *, and pyrolytic plating.

The result of the survey and search is that there appears to be a startling lack of information on beryllium CVD. There seems to be a comparative abundance, of CVD information on just about every other element except beryllium. The concensus is that beryllium metal cannot be chemically-vapor deposited rapidly or efficiently by any known method for the following reasons:

1 Beryllium compounds, particularly the inorganic halides, oxides, carbides, and hydrides, are extremely stable at temperatures up to and often exceeding the melting point of beryllium metal itself 2332°F (1277°C).

2 Beryllium metal has an appreciable vapor pressure over 1652°F (900°C) which works against deposition of the metal.

3 The chemical reactivity of beryllium metal toward most other elements (the inert gases being the probable exceptions) and most other compounds (beryllium oxide, calcium oxide, zirconium oxide the most notable exceptions) requires an extremely careful control of the vapor-deposition atmosphere.

Four good abstracts and bibliographies were found. These, with comments, are as follows:

1 White, D. and Burke, J., "The Metal Beryllium," American Society For Metals, 1955

* The preferred description for this method appears to be "chemical-vapor deposition (CVD)" with "physical vapor deposition" applicable to vacuum deposition.

Although comparatively old (1955) this book still contains much useful information descriptive to beryllium technology. Chapters titled "Reduction, Fabrication, Properties, The Brittleness Problem, Metallography, Corrosion, and Health Hazards" are of particular interest.

There are no references to CVD of beryllium.

2 Powell, Campbell, and Gonser, "Vapor Plating," John Wiley and Sons, 1955

This book is a good state-of-the-art report for CVD up to 1955. Beryllium CVD's are described with relevant references. Prior to 1955 the basic metal compounds for CVD's were primarily the halides. The halides of beryllium, however, are extremely thermally stable. High thermal stability (of the halides), an appreciable high vapor pressure of beryllium metal at temperatures above 1800°F (985°C), and the high chemical affinity of beryllium metal for other materials (elements and compounds) work against beryllium being a good candidate for chemical-vapor deposition (CVD) †.

Six references are given for CVD of beryllium coatings from the halides. The deposits were generally of low quality and contaminated from glassware container walls or from foreign impurities present during the deposition.

Although beryllium metal is difficult to CVD, beryllium compounds (oxides, carbides, borides) are not as difficult; the method being to react the vaporized halide with an even more reactant element, e.g., oxygen; the reaction being a displacement mechanism.

3 "Bibliography and Abstract: Plating By Thermal Decomposition," Hoyle, Dr. R., Plating, Nov 1962; Dec 1962; Jan 1963; Feb 1963

Very good reference article. Bulk of references published 1955 - 1962. Here again there is a paucity of information on beryllium with respect to CVD. Six references are listed:

a van Arkel, A. E., "Production of High Melting Metals By Thermal Dissociation," Metallwirtschaft, Vol 13, No. 405, p 511 (1934).

† In 1955 chemical-vapor deposition (CVD) usually centered around hydrogen reduction or thermal decomposition of the metal halides or hydrides. Metal-organics compounds, with their generally much lower decomposition temperatures, were unexplored.

b Bulloff, J., "Cleaning and Coating of Aluminum With Metals," U.S. 2,898,230 (August 4, 1959)

c Kopelman, B. and Bender, H., "The Dissociation of Beryllium Iodide in Platinum Containers," Journal of Electrochem Society, Vol 98, (1951)

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f Sloman, H., "Research on Beryllium," Journal Institute of Metals, Vol 49, (1932).

These references were examined. The results were that the beryllium deposit generally was unsatisfactory, i.e., no metal deposited and/or a large amount of deposited impurities, probably beryllium oxides or carbides.

4 Blocher, J., "Selected CVD Information Developed at Battelle in 1962-1963," Nov 18, 1964, Battelle Memorial Institute

Information includes an impressive number of annotated literature references (more than 500) published in years 1961-1963. There is not one reference to beryllium CVD.

There are a number of recent magazine articles discussing beryllium a as a material for structural applications. The subject of CVD is not mentioned. The articles are included for general reference only:

1 Kelly, R., "Beryllium Structures," Space/Aeronautics, pp 64-71, July 1964

2 "Direct Rolling Makes Ductile Beryllium," Iron Age, p 127, March 4, 1965

3 Jennings, C., "What to Consider When Applying Beryllium," Metal Progress, pp 104-108, May 1965

4 Maas, M., "Beryllium," Design Engineering, pp 78-81, August 5, 1964

III. CONCLUSIONS

Information on chemical-vapor deposition of beryllium metal is extremely scarce. What information is available, dates from 1958 back and usually refers to CVD attempts using beryllium halides (the general opinion being that this approach is unsuitable due to the halides high thermal stability).

CVD references past 1958, particularly using beryllium metal-organics, are apparently proprietary information and generally remain unpublished.

IV. RECOMMENDATIONS

Chemical-vapor deposition (CVD) of beryllium metal should be extended into the beryllium metal-organic compounds. Herbert Kaufman in his book "Handbook of Organometallic Compounds" (D. Van Nostrand Co., Inc., 1961, 1600 pages) lists 30 such beryllium metal-organics, together with their physical properties and references (pages 24 to 28).

Appropriate safety precautions would have to be observed due to the high toxicity of beryllium materials particularly with the large surface to mass ratio of vaporized materials.

A successful CVD will depend basically on two mechanisms:

1 A "clean" breaking of the metal-organic molecular bond exactly between the metal and the organic. This allows the metal to deposit free of any inclusions, e.g., oxides, carbides, etc.

2 Control of foreign impurities both in the starting materials (metal-organic, carrier gases) and in the CVD environmental system, i.e., surface and volume cleanliness of the entire system: walls, specimen, etc.

The present methods for chemical-vapor deposition are usually pyrolytic decomposition and/or hydrogen reduction. These mechanisms are satisfactory for some of the simplier CVD elements, such as nickel plating from nickel carbonyl, but much more is desired for the more reactive metals: beryllium, titanium, tantalum, etc., in order to increase deposition rates and pure metal yields. Catalytic studies both in carrier gases such as H_2S supposedly benefits nickel deposition from the nickel carbonyl-CVD; the use of electrical corona*; and also of an electrostatic "flip-flop"

*Coffman, J. and Browne, W., "Corona Chemistry," Scientific American, pp 91 to 97, 1965.

("+" to "-") polarization of the work to remove gases absorbed on the work surfaces. These gases are often highly absorbed on the work surface virtually stopping the plating deposition unless higher temperatures are applied to the work. The electric discharge that results from the incomplete breakdown of a gas can be put to work as a chemical catalyst. The corona acts by creating numerous free radicals that mediate chemical reactions.

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APPENDIX C

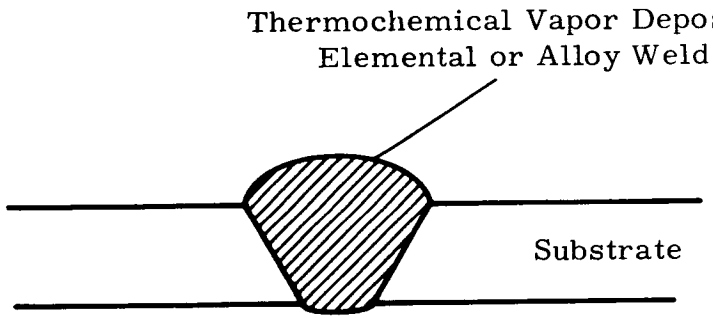
PHASE II STAINLESS STEEL ALLOY 321

SUMMARY

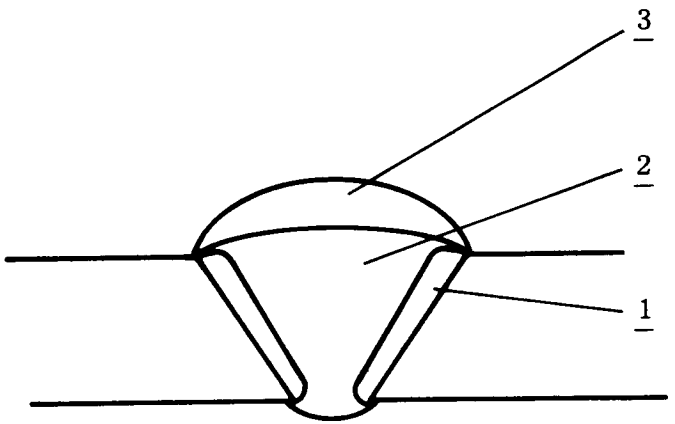
A program directed toward the welding of stainless steel alloy 321 below its recrystallization temperature was conducted using thermochemical vapor deposition (TCVD) techniques. This feasibility study resulted in the development of techniques for the deposition of elemental nickel, elemental iron, and binary alloys of nickel and iron on stainless steel. The techniques are based on the thermochemical decomposition of nickel tetracarbonyl and iron pentacarbonyl either separately (for elemental depositions) or simultaneously (for alloy depositions) in the temperature range of 400 to 800°F. The room temperature properties of the 321 stainless steel are not affected when held in this temperature range for periods up to 2 hours. Actual weldments were achieved with chemical and metallurgical quality sufficiently high to warrant further development of the process.

This process, when fully developed, should find application in the repair and fabrication of orbiting space platforms and space vehicles, as well as in situations where conventional welding temperatures cannot be tolerated (see Conclusions and Recommendations).

The development of thermochemical vapor depositions (TCVD) of nickel-iron-carbon alloys for structural weldments is a completely new technology. Pure elemental nickel and pure elemental iron coatings have long been available through electroplating, physical (vacuum) vapor deposition, and thermochemical vapor deposition methods. The concept of plating nickel-iron-carbon alloys for high strength weldments is completely new. Pure nickel deposits display toughness to impact, but are of low structural strength while iron-carbon deposits are exactly the opposite, i.e. very brittle, non-tough, non-impact resistant, but of high intrinsic structural strength (Rockwell C hardness 65). By process control of nickel and iron carbonyl flowrates, a wide range of Ni-Fe-C alloys can be thermochemical vapor deposited (TCVD), with mechanical and physical properties tailored to a variety of engineering requirements. These are typically illustrated by the following sketches:



Homogeneous Noncomposite Structure



Hetergeneous Noncomposite Structure

PURPOSE

Phase II, part of a four phase NASA sponsored program to determine the feasibility of joining metals by use of thermochemical vapor deposition reactions, concerns the joining of the stainless steel alloy 321; the emphasis being on the development of techniques for making high strength, impact-resistant (tough) depositions suitable for structural joint weldments.

SCOPE

Phase II concerns the development of process procedures for the deposition of elemental nickel, elemental iron, and binary alloys of nickel-iron-carbon from the thermochemical decomposition of suitable nickel and iron compounds; and having achieved satisfactory deposition, make and evaluate simple welds.

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I. TECHNICAL APPROACH

As described in the fifth monthly status report of this contract, the selection of a suitable TCVD iron plating compound was narrowed to the iron pentacarbonyl after considering the iron halides and other organometallics, i.e. dicyclopentadienyl iron (Ferrocene) (see Appendix A, Table II). The halides were rejected basically due to high process and material decomposition temperature requirements; Ferrocene also turned out to be too thermally stable for TCVD iron yields.

Nickel (Reference 1) is readily deposited in an adherent, ductile form by thermal decomposition of nickel tetracarbonyl with optimum deposition temperatures from 356° to 392°F. Above 392°F (200°C) finely divided nickel is formed which catalyzes the disproportionation of CO, causing carbon to co-deposit with the nickel. The carbon, however, does not affect the mechanical properties of nickel; however, it does with iron forming steels, e.g. carbon exceeding 1.0 percent. Water vapor causes no catalytic effect on the decomposition mechanism but does adversely affect the stainless steel substrate, i.e. will repassivate it. For chemical kinetics, thermodynamics, catalysts, etc. refer to References 1, 2, 4, 5, 10, and 11.

Nickel can also be deposited at 662 to 842°F from nickel acetylacetonate vaporized at 320°F (160°C), preferably at reduced pressure.

Unlike the adherent, ductile nickel coatings obtained from the TCVD of nickel carbonyl, iron coatings from the TCVD of iron carbonyl are extremely brittle in the as-deposited state, due to co-deposited carbon in amounts up to 1.5 percent. To remove embrittling carbon requires extended heat treatments at 1000 to 1800°F for at least 20 to 30 minutes. Several annealings of this sort must be used in building up heavy coatings, since the brittle deposits tend to spall when they become more than a few tenths of a mil thick. It is apparent, with respect to TCVD joining objectives, that the use of such iron (steel) coatings must be restricted to thin coatings, as for wear resistance. Hard brittle Fe-C deposits are however, also useful as a hardening mechanism in strengthening the otherwise soft, ductile nickel coatings, i.e., alloy TCVD plating of Ni-Fe-C compositions displaying the desirable design requirements for structural joints (Figure 1) at a process temperature below the substrates recrystallization temperature.

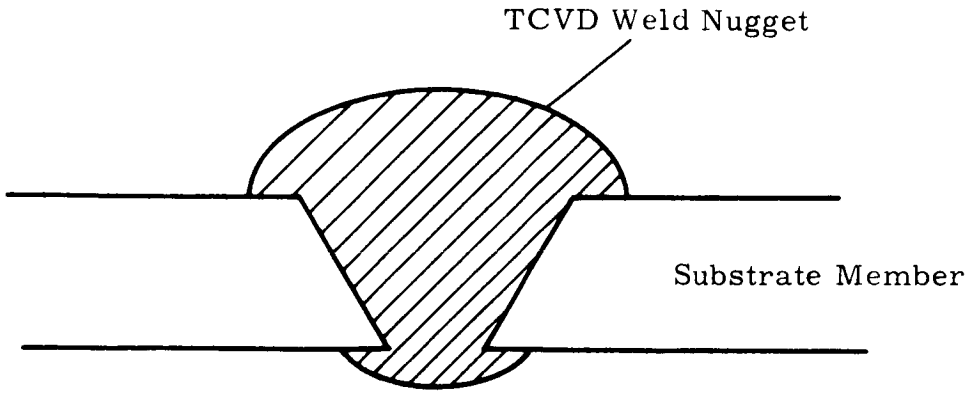


Figure 1. Typical TCVD Weldment

A. DESIGN REQUIREMENTS FOR STRUCTURAL JOINTS

1. Engineering Considerations

   1 Strength equal to or exceeding that of the members being joined

   2 Toughness (ductility) to resist impacts, thermal cycling, thermal shock, etc.

   3 Metallurgical electromotive compatibility to resist galvanic corrosion

   4 Metallurgical stability over service operating temperatures.

2. Metallurgical Considerations

   1 Adhesive strength - metallurgical bond, i.e. some mutual metal solubility of the TCVD deposit and the substrate without the formation of (detrimental) low melting point phases, brittle metallics, compatible coefficient of expansions

   2 Cohesive strength - high density, fine grain structure of controlled purity, uniformity; free from voids and/or microcracks.

B. TCVD PROCESS EVALUATION OBJECTIVES (Figure 2)

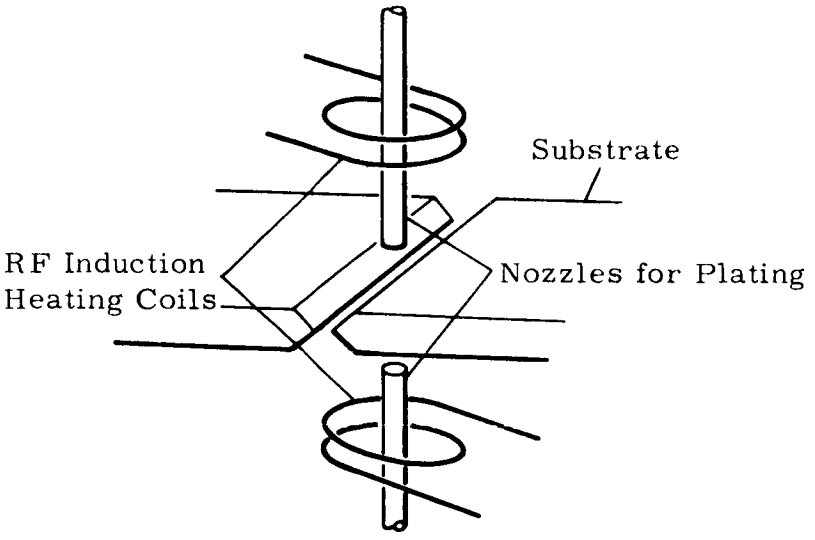


Figure 2. TCVD Process Evaluation

1. TCVD Plating Materials

   1 Readily vaporized, metered, and transported from plating generators, through process lines, nozzles . . . to the joint area.

   2 Possess decomposition products which are gaseous, easily analyzed, and uncomplicated by side reactions.

   3 Decompose over a short range of temperatures and produce a pure deposit, especially control of codeposited carbon.

4 Undergo thermal decomposition without chemical reaction with the substrate, e.g., sulfer or phosphorus TCVD compounds could embrittle the stainless steel.

5 Nontoxic, easily analyzed, high-purity, low cost.

2. Engineering Considerations

1 Strength

2 Toughness

3 Galvanic corrosion resistance

4 Metallurgical stability.

3. RF Induction Heating

Localized uniform heat to confine weld deposit to joint i. e., control of hot and cold spots which cause TCVD defects such as nodules, craters, plateau, voids, etc.

4. Environment

1 Vacuum - Suitable for treatment of substrate, i.e., 10^{-4} torr or better

2 Purity - Freedom from sulfur, phosphorus, H_2O, and O_2 which foul or embrittle substrate; preferably 10^{-6} torr or better; H_2O dew point -100°F maximum; O_2 less than 1 ppm.

5. Substrate Cleaning

Suitable for metallic bond to TCVD deposit, i.e., free from

1 Organics contaminants - grease, oils, moisture

2 Inorganic contaminants - oxides

3 Gases adsorbed on surface.

6. Nozzles

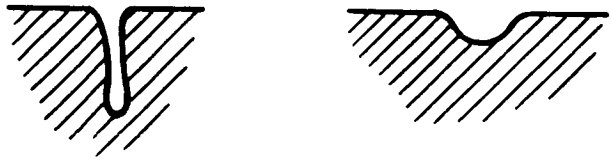
Nozzle configuration and angle to provide

1 Laminar uniform flow over joint to avoid turbulence

2 Confine weld to joint area.

7. Joint Geometry

The joint geometry must be suitable to allow the full throwing power of the plating compound, i.e., must have free entrance and exit.



Poor Good

Typical Joints

Preferred

Butt Single Bevel Double Bevel

C. TCVD PARAMETERS

An ideal TCVD joining process should require only a short time to complete and should yield joints with strengths and ductility equal to or exceeding that of the members being joined. The process itself should possess excellent microthrowing power, i.e. it should be possible to deposit the bonding medium in sharp corners or in recesses and to bridge gaps between the members being joined.

An elaboration of the following TCVD parameters is appropriate for TCVD Weld Design and TCVD Process Evaluation:

1 Plating compound selection

2 Environment control

3 Substrate material

4 Substrate joint geometry

5 Substrate heating

6 Carbonyl vapor generation, flow, and control

7 Process procedure.

1. Plating Compound Selection

Two important considerations in the selection of a TCVD plating compound are:

1 Be able to yield a TCVD deposit capable of meeting engineering requirements (strength, toughness, corrosion resistance, thermal shock and cycling resistance, metallurgically stable at service temperatures, etc.)

2 Should lend itself to ready process control (Reference 2); easily vaporized at low temperatures, decompose over a short range of temperatures, easily metered, high purity, low cost, non-toxic, etc.

The carbonyls of iron and nickel meet most of the important considerations (Tables I and II). Their main deficiency is that neither, by itself, will meet the engineering requirements. Both carbonyls must be used simultaneously to TCVD out a Ni-Fe-C alloy that can meet the engineering requirements:

Nickel, pure, elemental deposits	Soft, ductile, tough but low structural strength.
↕ Wide range of possible nickel-iron-carbon alloys	Wide variety of Ni-Fe-C alloy compositions provide variations of weld joint toughness and strength, including composite structures.
Iron, (steel) elemental, containing minimum of 0.7 percent carbon	Very hard, intrinsically very high structural strength, but extremely brittleness (thicknesses build-up limited to 2 to 3 mils unless extensively heat treated).

TABLE I

Physical Properties of Iron Carbonyl*

Formula	$Fe(CO)_5$
Molecular weight	195.9
Purity	Technical grade, better than 99.5 percent iron pentacarbonyl; practically free from other metals, containing traces of nonacarbonyl and iron oxide.
Appearance	Yellow to dark red colored liquid.
Specific gravity	t°C = 0 20.0 21.1 40 80 sp gr = 1.494 1.459 1.457 1.433 1.351
Refractive index	$n_D^{22} = 1.519$
Critical temp	285-288°C. (545-550°F)
Critical pressure	29.6 atm
Boiling point (760 mm)	103°C (217.4°F)
Vapor pressure	t°C = -7.0 0.0 16.1 18.4 35.0 78.0 101.8 102.8 P(mm) = 14.0 16.0 25.9 28.2 52.0 133 736 749
Melting point	-20°C (-4°F)
Flash point	-15°C (5°F)
Specific heat	c = 0.288 cal/gram (liquid at 23°C) C = 56.7 cal/mol (liquid at 23°C) C_v = 43.3 cal/mol (vapor at 23°C)
Heat of formation	54.2 cal/mol (liquid $Fe(CO)_5$ from Fe + 5 CO at constant volume).
Heat of decomposition	46.5 cal/mol
Latent heat of vaporization	39.45 cal/gram

TABLE I (Cont)

Heat of fusion	3.25 ± 0.04 cal/mol	
Heat of combustion	384.5 ± 0.7 cal/mol	
Expansion coefficient	0-21°C	0.00121
	21-40°C	0.00128
	40-60°C	0.00142
Surface tension	2.24 mg/mm = 2.20 dynes/cm at 20°C	
Absolute viscosity	At 20.2°C 75.5 centipoise (H_2O, 100 cp = 0.00755 ($cm^1/gm/s^1$)	
Dielectric constant	2.2	

* See Reference 3

TABLE II

Physical Properties of Nickel Carbonyl*

Formula	$Ni(CO)_4$
Molecular weight	170.75
Vapor pressure at 68°F	315 mm Hg
Boiling point at 1 atm	109.8°F (43.2°C)
Freezing point at 1 atm	-13°F (-25°C)
Specific gravity, liquid at 17°C	1.3186
Critical temperature	392°F (200°C)
Critical pressure	441 psia (30 atm)
Critical density	0.46g/mil
Latent heat of vaporization at bp	38.1 cal/g
Surface tension at 20°C	15.88 dynes/cm
Trouton constant	20.6

*See Reference 4

The basic TCVD process considerations are as follows:

1 Readily vaporized, metered, and transported from plating generators, through process lines, and nozzles to the joint area

2 Possess decomposition products that are gaseous, easily analyzed, and uncomplicated by side reactions

3 Decompose over a short range of temperatures and produce a high purity deposit; especially with control over co-deposited carbon (undesirable)

4 Undergo thermal decomposition without chemical reaction with the substrate, for example, sulfur, carbon, and phosphorous TCVD compounds usually embrittle stainless steels at elevated temperatures

5 Non-toxic, easily analyzed, high-purity, low cost.

TCVD deposits of nickel and iron are metallurgically compatable with 321 stainless steel substrates. Carbonyl plating compounds are sulfur, phosphorous, and oxygen free, i.e. they do not embrittle stainless steels at elevated temperatures. Carbon co-deposited with both nickel (up to 0.4 percent) and iron (typically 0.5 to 2.0 percent) could be a problem at elevated temperatures from the effect of chromium carbides.

Usually small amounts of oxygen and moisture (present as air leaks) are not detrimental to the chemical TCVD but they could have the tendency to repassivate stainless steel surfaces should they be used. (Nickel electroplate pretreatment to TCVD is recommended).

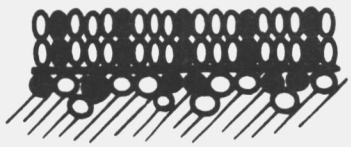
Table III describes the material used during TCVD experimentation.

2. Environmental Control

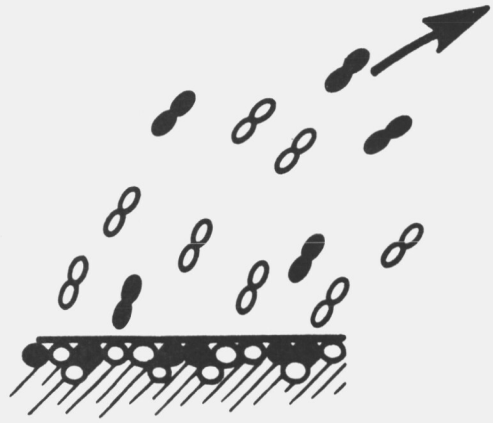
The environmental control around TCVD process equipment (Figure 3) is determined by the vacuum and contamination control requirements.

a. Vacuum Requirements (10^{-4} torr, minimum)

In addition to adequate cleaning, substrates require degassing to remove absorbed air molecules to obtain metallurgical bonding.



Substrate surface chemically cleaned of oil, grease dirt, oxides, etc. Sketch shows adsorbed air and moisture molecules.



Degassed surface, baked at 800°F at 10^{-4} torr. Sketch shows atoms of chromium, nickel, and iron exposed at surface with no adsorbed gas residues.

TABLE III

Materials Used During TCVD Experimentation

Material	Application	Description
Nitrogen	Purging gas	Extra dry, dew point at -93°F (4ppm). Source: American Cryogenics
Helium	Purging gas	High purity (most all grades are high purity - filled at helium fields in Texas). Source: American Cryogenics
Hydrogen	Reduction of nickel oxides	99.995 percent pure. Source: American Cryogenics
Iron pentacarbonyl	Fe-C TCVD source	Technical grade, better than 99.5 percent iron pentacarbonyl; practically free from other metals, containing traces of nonacarbonyl and iron oxide. Source: Antara Chemicals
Nickel tetracarbonyl	Nickel TCVD source	99 percent minimum purity. Source: Research Inorganic Chemical

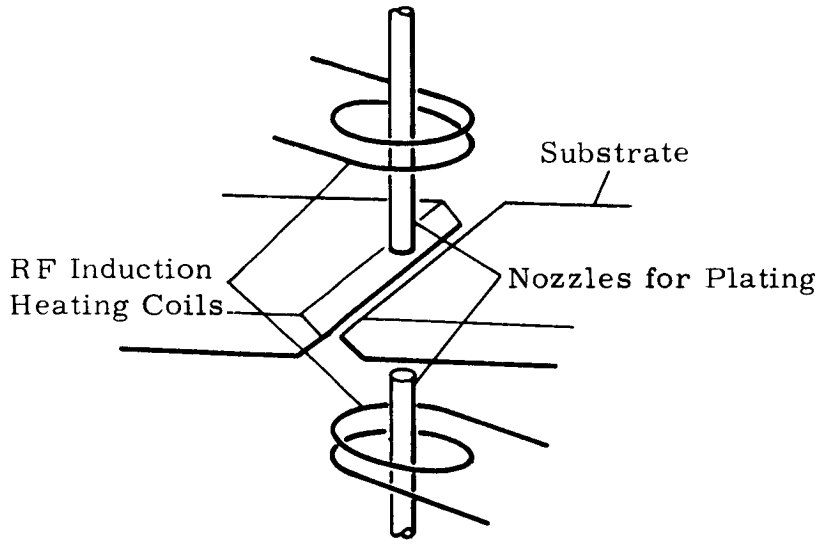


Figure 3. TCVD Environmental Control

b. Contamination Control Requirements

In addition to the vacuum requirements for degassing the substrate, environment contamination, including air leaks, carrier gases, and outgassing, must be controlled to prevent repassivation (particularly activated stainless steels) or embrittlement, as follows:

1 Moisture: dew point of -100°F maximum

2 Oxygen to 1 ppm maximum*

3 Complete exclusion of detrimental elements such as sulfur or phosphorous (embrittle stainless steels)

4 Carbon deposition control particularly on non-stabilized grades of stainless steel.

* Stainless steels activated and nickel electroplated require less stringent environments: e.g. O_2, 2 ppm max; moisture, -60°F dew point max

3. Substrate Material

The metal-metal oxide equilibrium in hydrogen atmospheres (Figure 4) clearly indicates the problem of maintaining stainless steels surfaces in the active state necessary for a metallurgical bond to the TCVD deposit. The metallurgical bond requirements for the stainless steel substrate are shown in Figure 5 in which the TCVD nickel atoms are directly in contact with stainless steel atoms, with no (passivated) oxide layer interface.

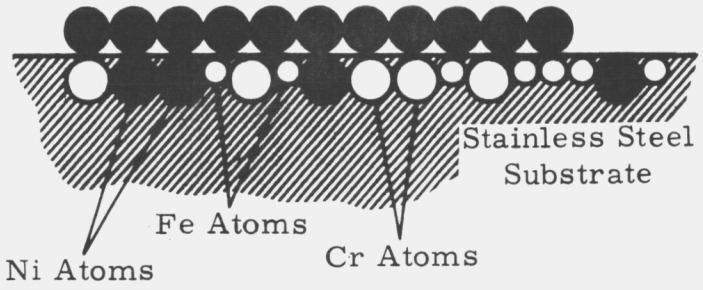


Figure 4. Metal-Metal Oxide Equilibriums in Hydrogen Atmospheres

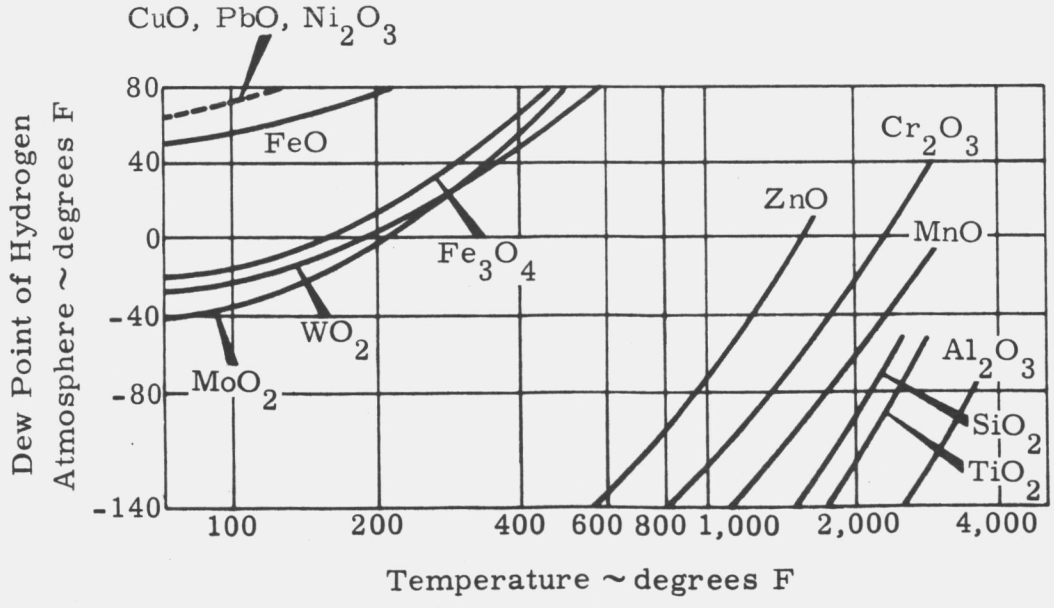


Figure 5. Stainless Steel Substrate

The metal oxides of iron, copper, lead, nickel, and even molybdenum and tunsten are vastly more easy to reduce at low temperatures and at high dew points than zinc, chromium, manganese, silicon, titanium, and aluminum (Reference 5). The element chromium makes hydrogen reduction activation of stainless steels impractical with respect to TCVD objects, i.e., activation requires heating the substrate to high temperatures (1800°F) using palladium purified hydrogen to control oxygen contamination to 1 ppm, maximum, and moisture control to a dew point of -75°F maximum. The temperature of 1800°F approachs the annealing temperatures of the stainless steel substrate.

From Figure 4, nickel however is comparatively easy to reduce by heating to 800°F in hydrogen, dew point of -40°F or better. (Moisture control to dew points on the order of -100°F require extra care in process control: baked system chamber and process lines, efficient dessicants, liquid nitrogen cold traps, etc.) The best approach, therefore, is to activate and electroplate the stainless steel with a soft, ductile nickel (such as from a nickel sulfamate bath) to approximately 0.00005 inch thick. Nickel oxide films forming on the electroplated nickel are easily reduced by hydrogen gas treatment at 800°F, in vacuum (the temperature ordinarily used for degas treatments).

The cleaning procedures used on the substrate material are presented in Table IV.

TABLE IV

Experimental Cleaning Procedures Used on Substrates

Procedure 1

Step a Solvent clean (trichloroethylene vapor degrease)
Step b Alkaline clean (hot)
Step c Hydrochloric acid (20% by volume); room temperature cathodic treatment for 4 minutes at 5 A/ft^2.

Procedure 2

Repeat steps a, b, and c of Procedure 1
Step d Nickel electroplate at 30 A/ft^2 for 6 minutes (sulfamate nickel plate SN)

4. Substrate Joint Geometry

The steps required in the formation of a metallurgical bond by thermochemical vapor deposition (TCVD) of nickel tetracarbonyl are shown in Figure 6. The new nickel carbonyl molecule must penetrate a vast number of carbon monoxide molecules being liberated from the TCVD chemical reaction. Upon penetrating to the substrate the nickel carbonyl liberates its own carbon monoxide molecules and deposits as a nickel atom.

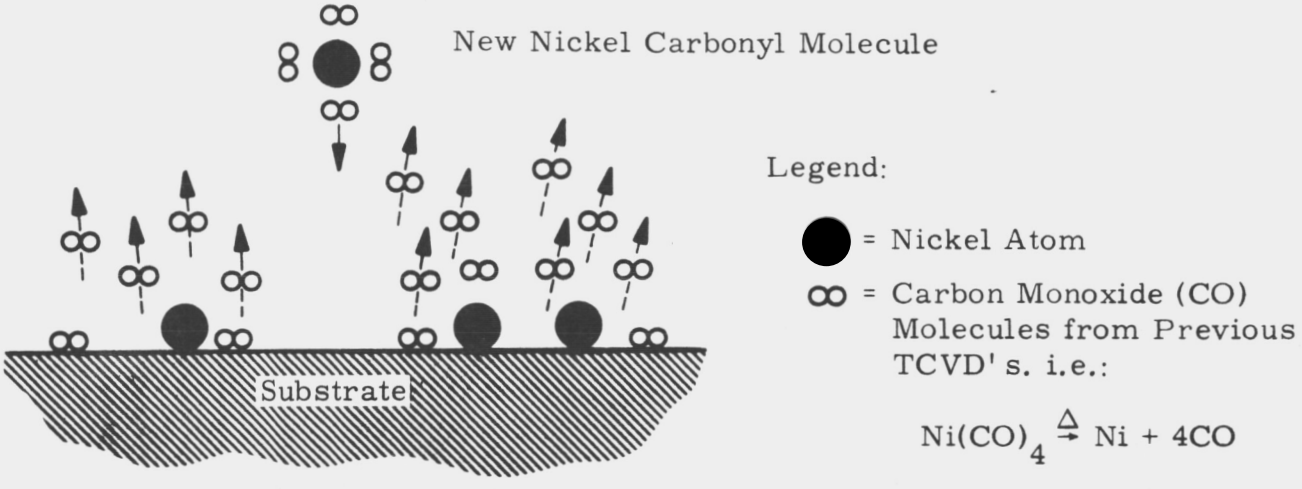


Figure 6. TCVD of Nickel Tetracarbonyl

The carbon monoxide causes two real problems: 1) an adverse effect on the metallurgical bond (poor adhesion) and 2) serious throwing power deficiency necessitating design of the joint geometry.

In the metallurgical bond problem (Figure 7) some of the carbon monoxide molecules escape but others are caught at the deposition surface. TCVD nickel continues to build up on the adsorbed carbon molecules resulting in a low strength, low density carbon monoxide-nickel interface which subsequently loses adhesion to the substrate, i.e., blisters and peels from the substrate.

This problem is corrected by first degassing the substrate free of adsorbed air molecules; depositing a TCVD nickel flash plate approximately 0.00005 inch thick; and degassing again to remove the carbon monoxide molecules adsorbed at the TCVD deposited/substrate interface. For technical purposes, the TCVD process should be interrupted frequently for carbon monoxide molecule degassing but in practice this is accounted for by the use of as high vacuums and temperatures as possible and still be within the TCVD engineering design limits of low temperature substrate exposures.

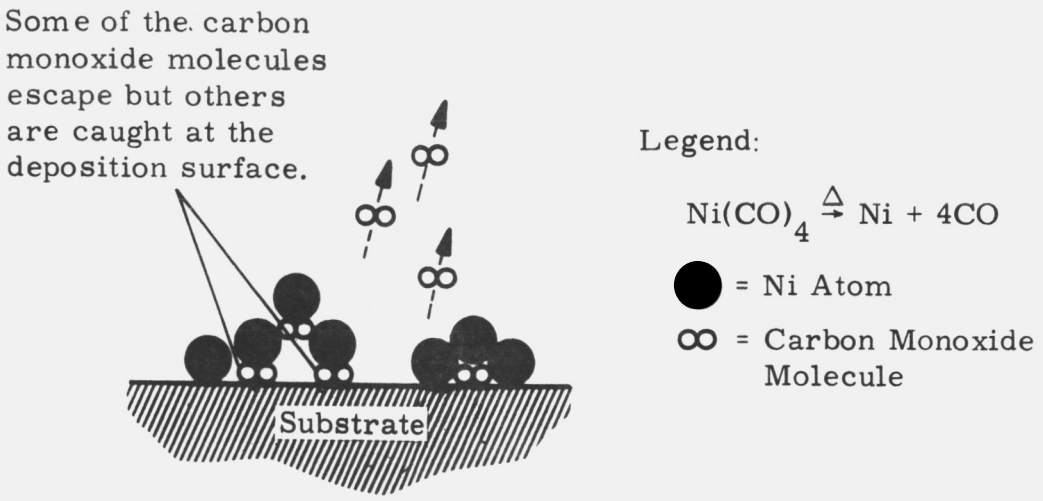


Figure 7. Metallurgical Bond Problem

The second problem (Figure 8) is even more acute. Carbon monoxide molecules can leave the nickel atom site via many directions. Actually many nickel carbonyl molecules are TCVD depositing simultaneously. The large evolution of carbon monoxide molecules greatly crowds the avenues of escape. Still, the illustration is approximately true.

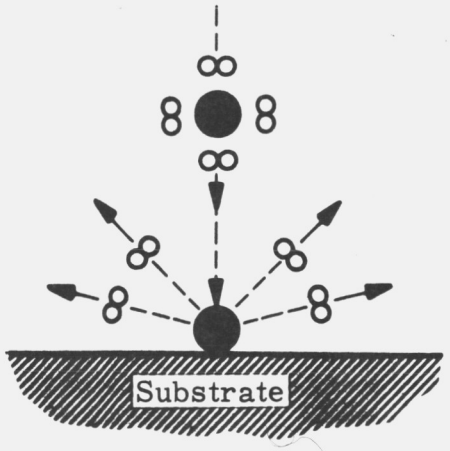


Figure 8. Nickel Carbonyl Molecules TCVD Depositing

Consider, however, the problem of a small hole or microcrack (Figure 9) within the substrate. For every atom of nickel deposited in the hole or microcrack, a 4:1 ratio of the number of molecules of carbon monoxide to nickel carbonyl molecules must come out to allow for the entrance of the next nickel carbonyl molecule. The "gushing out" action of the carbon monoxide makes it difficult for new nickel carbonyl molecules to enter; as a result the microhole does not fill as readily as the top substrate.

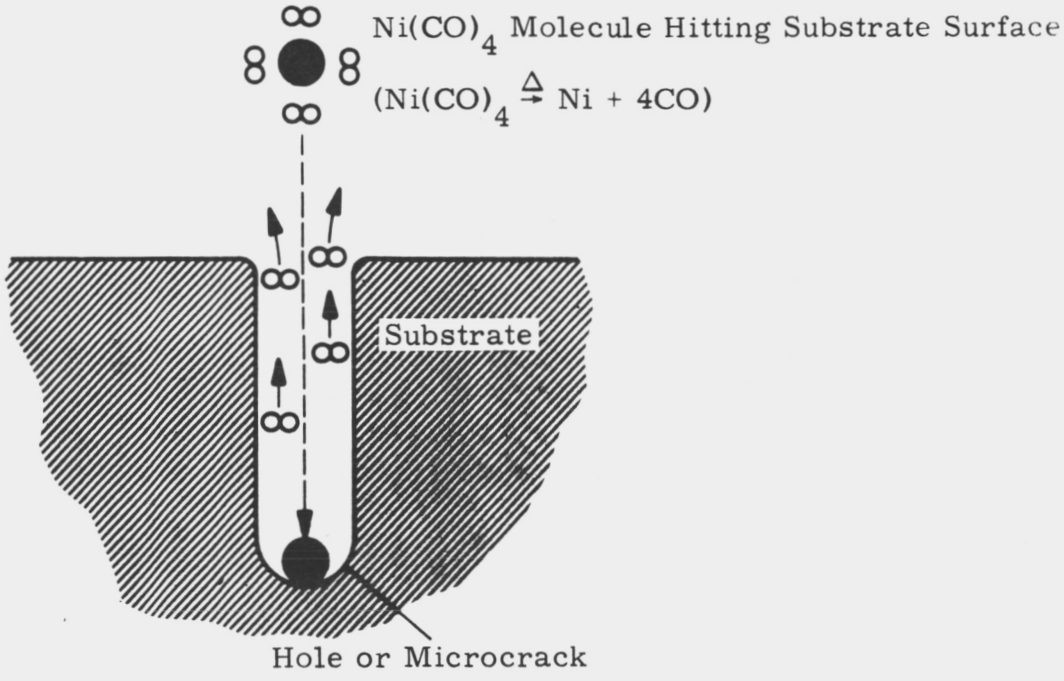
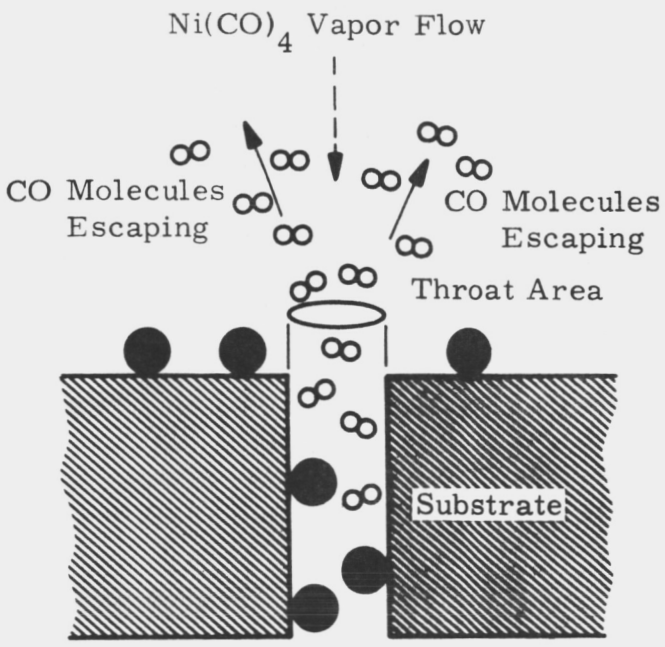


Figure 9. Microcrack Problem

The combination of a large amount of carbon monoxide molecules flowing in a direction opposite to that of the nickel carbonyl molecules, plus the fact that the microcrack offers a large surface area to which these carbon molecules become strongly absorbed, work against the TCVD mechanism reaction filling in the hole or microcrack.

A flat surface is readily TCVD deposited, i.e., carbon monoxide molecules free to escape in many directions, and a gradually curved surface is also readily TCVD coated. However consider the case of a straight butt joint. During the initial deposit (Figure 10) the throat of the butt weld is sufficiently open to allow the escape of the carbon monoxide molecules. In the intermediate deposition stage (Figure 11), similar to the electroplating

Initial Deposit

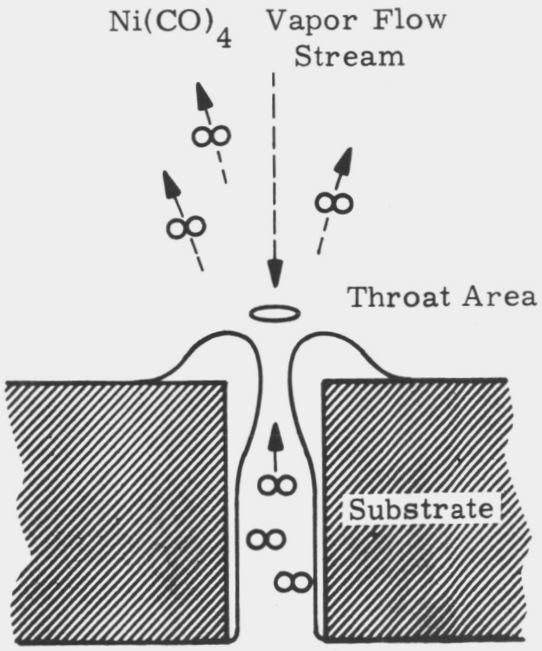


Note: The throat of the butt weld is sufficiently open to allow the escape of the carbon monoxide molecules.

$$Ni(CO)_4 \overset{\Delta}{\rightleftharpoons} Ni + 4CO$$

Figure 10. Initial Deposit of Nickel Carbonyl

Intermediate Deposition



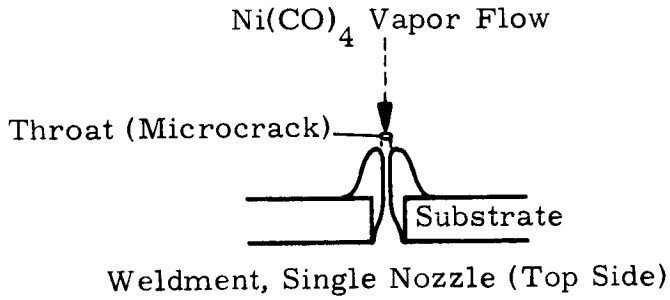
Note: Similar to the electroplating phenomena, substrate surfaces closest to the TCVD plating material are exposed to the richest supply of TCVD metal atoms and also are in best location for ready loss of carbon monoxide molecules; resulting in rapid buildup of surface edges and a rapid decrease of buildup inside of holes and crevices.

Figure 11. Intermediate Deposit of Nickel Carbonyl

phenomena, substrate surfaces closest to the TCVD plating material are exposed to the richest supply of TCVD metal atoms and also are in best location for ready loss of carbon monoxide molecules. This results in a rapid build-up of surface edges and a rapid decrease of build-up inside of holes and crevices.

In the final deposition stage for a single nozzle (Figure 12), the throat of the butt weld is essentially closed (actually a microcrack) through which passage of fresh nickel carbonyl molecules becomes almost impossible. Where depositions are made on both sides of the joint, i.e., double nozzles (Figure 13), the problem still remains acute. Not only does the microcrack limit the fresh supply of nickel carbonyl from penetrating into the microcrack, but the large volumes of carbon monoxide molecules rushing counter current to the nickel carbonyl molecules hinder depositions (micro-throwing power).

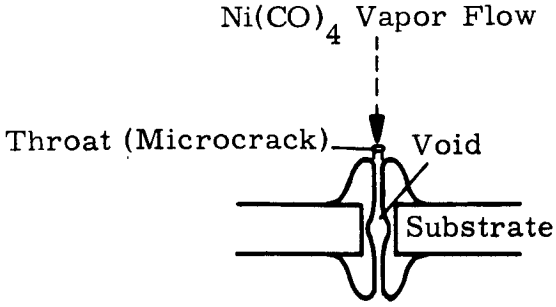
Final Deposition



Weldment, Single Nozzle (Top Side)

Note: The throat of the butt weld is essentially closed (actually a microcrack) through which passage of fresh $Ni(CO)_4$ molecules becomes almost impossible. Where depositions are made on both sides of the joint i.e. double nozzles the problem still remains acute.

Figure 12. Single Nozzle Weldment



Note: Not only does the microcrack limit the fresh supply of $Ni(CO)_4$ from penetrating into the microcrack; but the large volumes of carbon monoxide molecules rushing counter current to the $Ni(CO)_4$ hinder depositions (microthrowing power).

Weldment, Double Nozzle (Both Sides) Simultaneously

Figure 13. Double Nozzle Weldment

To effect structural joints, the configuration must allow ready entrance of fresh nickel carbonyl vapor and free, ready exit of the waste carbon monoxide molecules. Ideally TCVD plating compounds should consist of almost all metal with very little other fractions, e.g., carbon monoxide molecules. Ideally iron carbonyl should be Fe CO (actually it is Fe $(CO)_5$) and nickel carbonyl should be NiCO (actually it is $Ni(CO)_4$).

To deposit one atom of iron and one atom of nickel, nine molecules of carbon monoxide must be withdrawn free from the weld area. Weld joints must be opened-up with various bevels to allow the escape of these carbon monoxide molecules and to readily admit fresh molecules of TCVD plating compounds. As cited by Disckind (Reference 6) "Joint geometries are critical in obtaining sound deposits. High depth to width ratios of butt joint gaps do not appear to be feasible. With depositions from both sides and double V bevels, sound deposits can be readily made."

Typical acceptable and unacceptable simple weld joint geometries are shown in Figures 14 and 15.

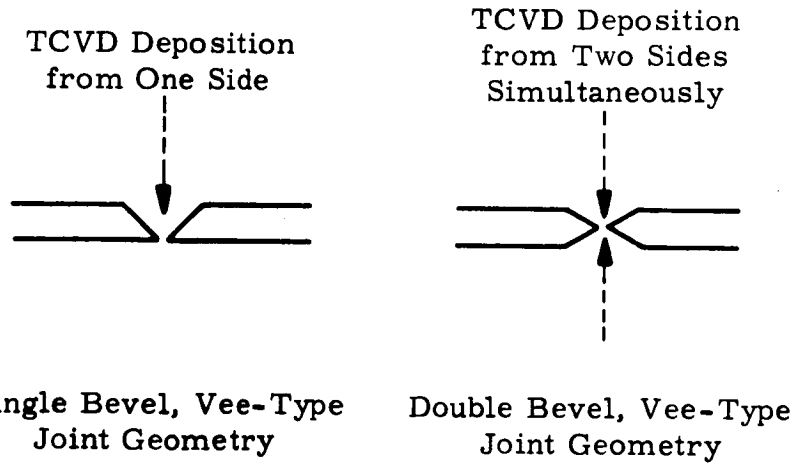
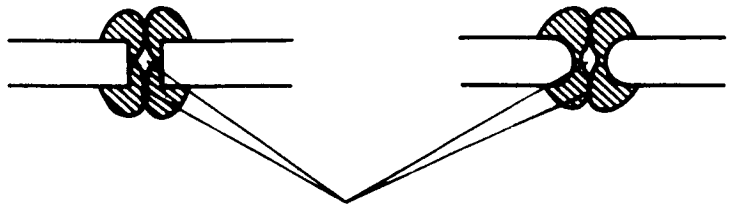


Figure 14. Acceptable Weld Joints



TCVD Tendency Forward Void
and Microcrack Formation

Figure 15. Unacceptable Weld Joints

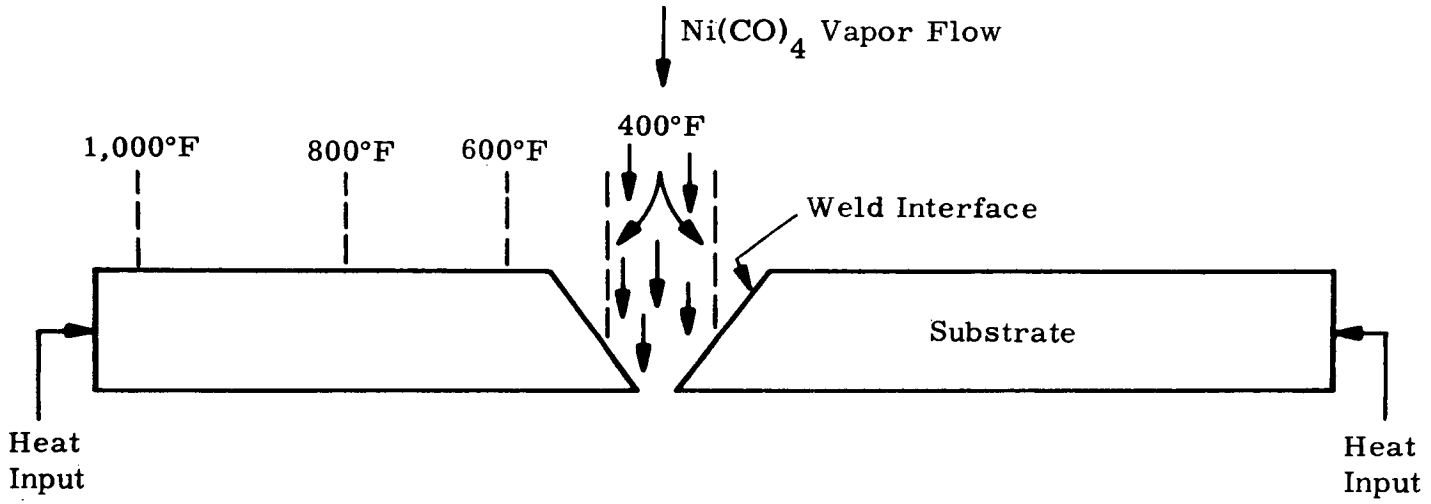
5. Substrate Heating

In general, substrate heating is a straight forward technique but not without problems. Direct resistance heating is not possible since the weld gap (joint) represents an electrical discontinuity. A heating element may be placed in juxtaposition with the substrate thereby heating the substrate by conduction. Other heating methods appear more direct. RF induction heating (too large and heavy for spare work) was used for this contract TCVD work.

The type and location of the heat input is especially important. Most of the previous TCVD have been concerned with coatings (Appendix C). Heat transfer requirements for coatings are comparatively low when compared to a nozzle blowing a fresh stream of the TCVD plating material against a substrate. The heating method selected must be capable of high heat inputs into the highly localized weld area. The same heat input to the entire weld piece would result in excessively high temperatures on other remaining weld substrate members (Figure 16).

6. Carbonyl Vapor Generation, Flow, and Control

Nickel and iron carbonyls, liquids at room temperatures, are easily vaporized at plating system vacuum pressures of approximately 1/2 mm Hg. Flowmeters are located immediately above the carbonyl generators (Figures 17 and 18). Carrier gases are not necessary to transport the carbonyl vapors to the plating chambers since the high vacuum downstream allows the carbonyls to exert their individual vapor pressures resulting in ready flows to the plating chamber. Various noble gases such as helium, argon, or nitrogen, deoxidized and dried, may be used for purging the plating system prior to the TCVD process run. Dry, deoxidized hydrogen is also valuable for reducing nonrefractory oxides of metals such as the electroplated nickel stainless steel substrate.



Note: If a heat input is supplied some distance from the weld interface, temperatures upstream could be much greater, perhaps even exceeding the recrystallization temperature (depending on the thermal conductivity of the substrate, TVCD flowrates chemical energy requirements, etc.).

Figure 16. TCVD Plating Compounds Impinging on Heated Substrate

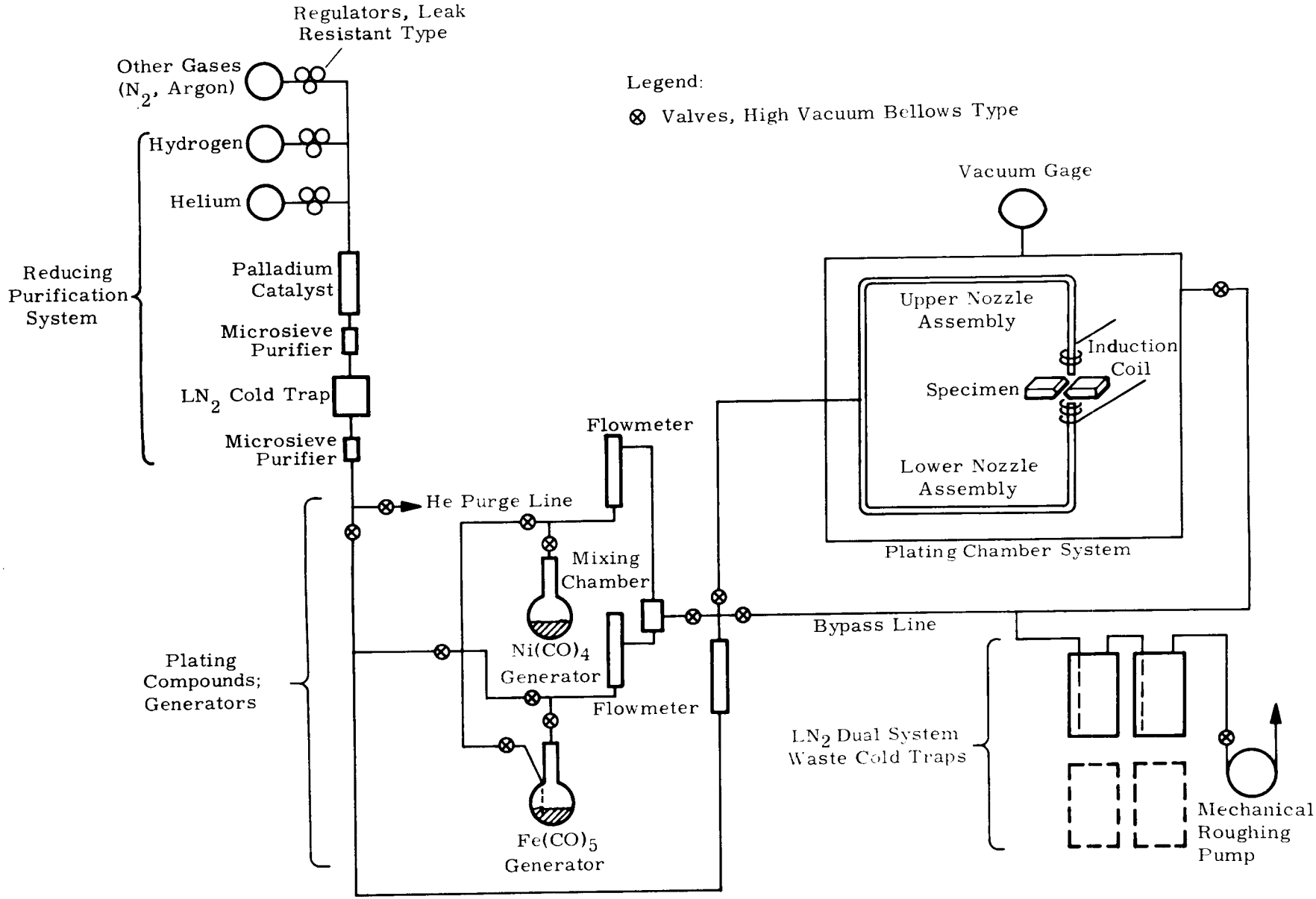


Figure 17. TCVD Process Schematic for Nickel-Iron-Carbon and Ni-Fe-C Alloy Depositions

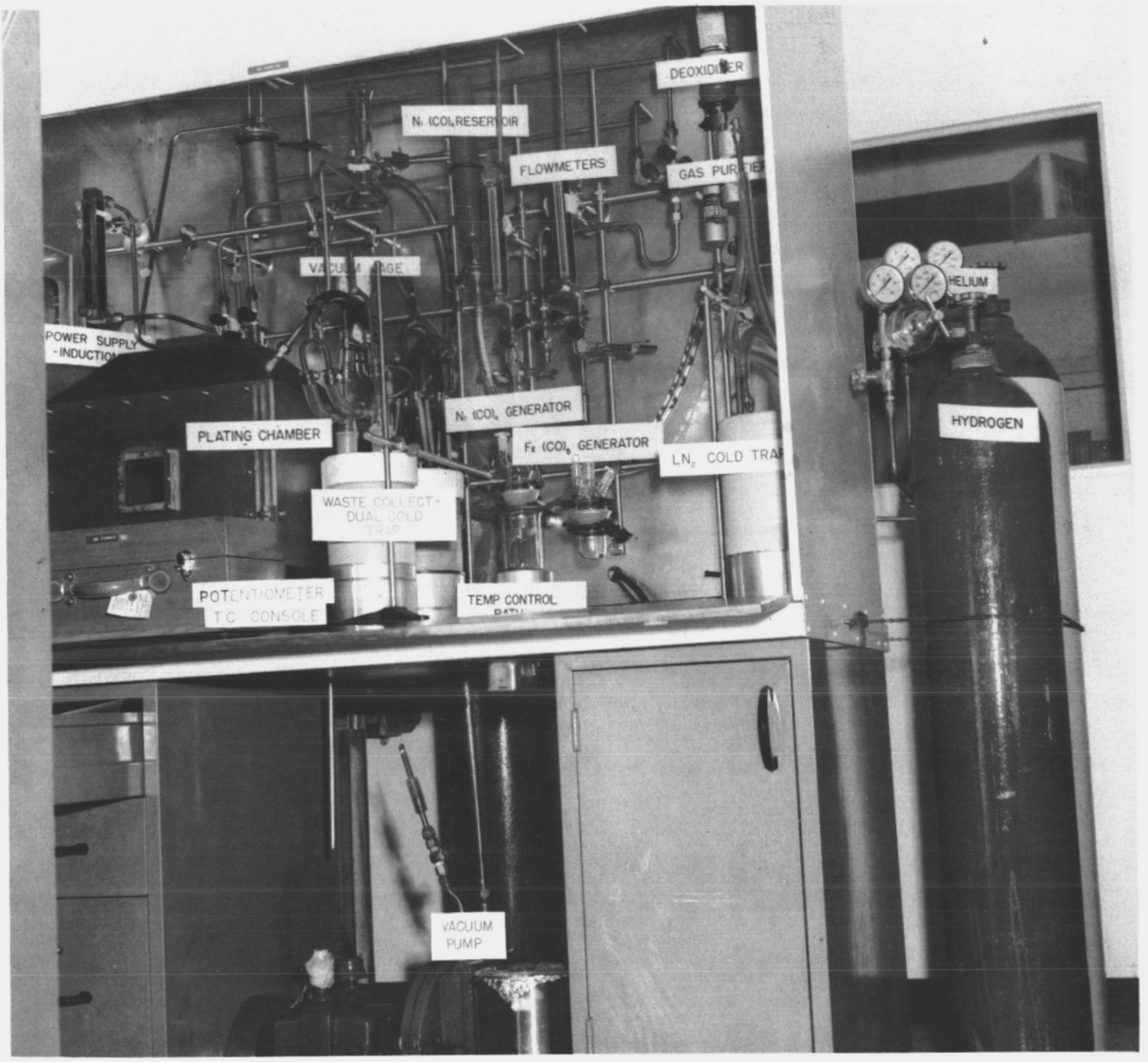


Figure 18. TCVD Apparatus

The TCVD plating system (chamber, process lines, etc.) can be constructed of most any material except various rubber compounds which are hardened and embrittled by carbonyl compounds. Metals such as copper, ceramics such as glass, plastics such as Teflon are all acceptable since within a short time such surfaces in contact with the TCVD vapors (particularly nickel carbonyl) become coated, i.e., with nickel. Such flows can be made directly to a cold trap and then to the nozzles for weldments. Nozzles exposed to electromagnetic fields such as in an induction field need to be water-cooled, i.e., TCVD deposits inside the nozzle becomes quite hot, thereby thermochemically reducing more of the carbonyl vapors eventually clogging the nozzle orifice.

7. Process Procedure

The stainless steel substrate is formed to one of the acceptable joint geometries previously described. The assembly is then cleaned, activated, and nickel electroplated (0.0001 to 0.0004 inch) using convention electroplating practices. A thermocouple is placed close to the weld area.

The assembly to be welded is placed into the vacuum system, beneath the water-cooled plating nozzles, with an RF induction coil located directly above and below the substrate joint. The environment is then evacuated to a minimum pressure of 0.1 microns (10^{-4} torr) with oxygen and moisture controlled to 1 ppm (or less) and a dew point of -60°F respectively. The substrate material is then degassed by heating, under vacuum, at 800°F for 15 minutes. A very low flow of helium/hydrogen mixture over the specimen helps in reducing the nickel oxides films on the substrate.

After degassing a thin flash or Ni-Fe-C alloy is applied by the thermochemical vapor deposition technique. Initial flows go through a chamber bypass (not through the nozzles) into a cold trap (when carbonyl flowrates have stabilized), valves are closed, and TCVD resumes. (Flash is approximately 0.0001 to 0.00005 inch.) Another degassing is used to remove carbon monoxide molecules from the $Ni(CO)_4 \overset{\Delta}{\rightarrow} Ni + 4CO_{(g)}$ reaction. This step is a requisite for subsequent good, adherent, blister-free TCVD.

After degassing TCVD plating of Ni-Fe-C alloy resumes until sufficient deposit has been made to make the weldment. (Typical deposition rates are from 0.025 to 0.050 inch per hour.)

Shutdown consists of shutting off the TCVD plating generators, flushing the nozzles with a helium/hydrogen gas mixture. The entire plating system is flushed with plant nitrogen to remove residual carbonyls. The RF induction heating is turned off and the specimen cooled to room temperature.

In the following paragraphs suggestions and recommendations to the process procedure are presented.

a. Substrate

As shown in Figure 4, some metals such as chromium (in stainless steels) form stable refractory oxides so quickly (less than 1/100 of a second) that conventional methods of cleaning and acid activation are somewhat inadequate, i.e., oxides reform in the several minute time period required to transfer the activate specimen to the plating chamber and to evacuate the plating chamber. Conventional cathodic treatment in hydrochloric acid so-

lution (20 percent by volume) and followed immediately with a ductile, low-stress nickel electroplate (such as a sulfomate nickel) provides an easily reactivated surface, i.e., reduction of nickel oxides with dry, oxygen-free hydrogen.

Sandblasting is not generally recommended. Too rough a sand grit may leave the substrate surface with micro-roughness-conducive to TCVD microcrack growth and leave silica (ro alumina) embedded into the substrate impairing subsequent TCVD adhesive bond.

b. Vacuum System Pressure

The plating chamber and process lines must be air-leak-tight to prevent reoxidation of the activated, hydrogen-reduced, electroplated nickel substrate during the 800°F degassing. Both low pressure (10^{-4} torr) and leak tightness are necessary. Baking and flushing of the chamber and process lines with dry, pure nitrogen, helium, etc., may be used as an aid in removing moisture and oxygen absorbed within the plating system.

c. Induction Heating

To prevent arcing and corona during induction heating of substrates, an RF stepdown transformer is desirable (voltages inside plating chamber should be under 20 volts) with a minimum number of coil loops, e.g., two loops over the specimen and two under the specimen are sufficient; the center loop also should be grounded thereby further reducing effective emfs by one-half. Noble gases such as argon, helium, etc., arc and/or corona more than the non-noble gases such as nitrogen and carbon dioxide. Both noble and non-noble gases are acceptable with respect to chemical reaction provided moisture and oxygen contamination can be controlled to the limits previously stated.

d. Nozzles

Metal, ceramic, of plastic nozzles are satisfactory; however, one basic problem arises when induction heating is used (Figures 19 and 20). The nozzles pass directly through the electromagnetic induction field. Ceramic (glass) or plastic (Teflon) nozzle materials are not affected and do not heat; however, soon after the flow of carbonyls through the process lines and nozzles has begun, a thin film of nickel and/or iron plates out. This metallic film quickly heats in locations close to the induction field (i.e., particularly the nozzles) quickly plugging up the nozzle orifice.

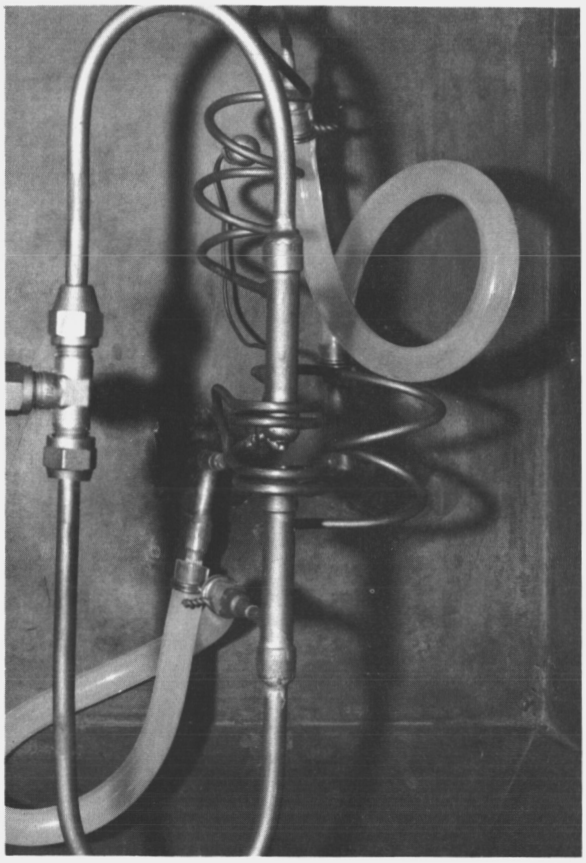


Figure 19. Water-Cooled TCVD Plating Nozzles and Induction Coil

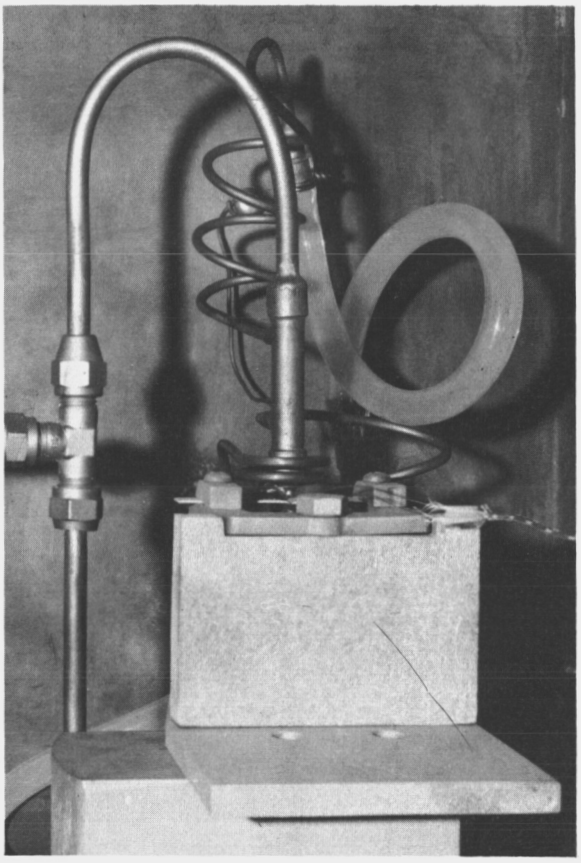


Figure 20. Water-Cooled TCVD Plating Nozzle, Induction Coil, and Specimen Holder/Specimen/ Thermocouple Assembly

The nozzle assembly was made by tapping water from the RF induction coil and insulating emf's from the coil through use of heavy wall vinyl tubing. (Vinyl has outgas tendency ruling against its use especially for higher vacuum work.)

e. Cold Traps

Carbonyls are readily soluble in most pump oils which causes three difficulties: 1) pump oils quickly become contaminated and present toxic vapor problems during pump servicing, 2) metal sludges form abrasively wearing close dimension pump parts, and 3) carbonyls exert high vapor pressures thereby impairing pump-down capability of subsequent process runs. Cold traps, particularly liquid nitrogen, are effective in removing these waste carbonyls before reaching the pump (Figure 17).

f. Safety

The carbonyls of both nickel and iron are very toxic as well as flammable when exposed to the atmosphere. Waste carbonyls should be burned before exiting to the atmosphere. Natural gas can be passed through the cold traps after most of the surrounding liquid nitrogen has left and the resulting mixture of natural gas and carbonyls burned in a high-temperature type gas burner (such as a Meaker Burner).

Ordinarily carbonyls present less hazardous problems with vacuum systems since system leaking is inward. (For other systems employing internal pressures exceeding atmospheric pressure, carbonyl process system chambers and lines must be leak-proof, i.e., leaks are outward.)

A transparent, clean burning flame will indicate the presence of leaking carbonyls above a concentration of 2 ppm. (A much better indicator kit, sensitive to one to two parts per billion, is available from the Matheson Corporation. This is the maximum allowable concentration in air set by the American Conference of Governmental Industrial Hygenists, April 1964, for repeated 8 hour daily exposures. Precautions in handling and storage, leak delection, materials of construction, etc., are described in detail (Reference 4). Diffusion pumps are used only during degassing treatments and never during plating because they are not needed and the oil contaminates easily.

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II. RESULTS

The research and development conducted demonstrates feasibility for the TCVD joining of type 321 stainless steel. Both high purity TCVD nickel and Ni-Fe-C alloys of a wide variety of compositions were achieved at rates to 50 mils per hour in the temperature range of 400 to 800°F with 600°F appearing optimum. Previous work by Owens, et al, (References 11 and 12) report optimum temperatures of 400°F for TCVD coatings. It is most important to note that weldments require a focusing of TCVD plating material to the joint. Subsequently heat transfer requirements demand heat transfer and higher temperatures of the substrate juxtaposition to the weld area. Above 800°F, the deposits become nodular, puffy and carbonaceous because of the premature chemical breakdown of the carbonyls; with the formation of mixtures of metals, carbides, and carbon. For clean activated stainless steel substrates, oxygen contamination must be less than 1 ppm and moisture controlled to a dew point of at least -100°F to prevent surfaces from repassivating. Other stainless steel substrates nickel electroplated before the TCVD, require far less stringent atmosphere control (i.e. oxygen several ppm; moisture -60°F maximum). Once the TCVD deposit has covered the substrate, oxygen and/or moisture contamination is less important.

Actual weldments have been made with satisfactory chemical and metallurgical bond. The tendency for the TCVD process toward leaving a microcrack (with a serious corresponding loss of joint strength) shown in Figure 21.

Table I, Appendix A, presents the experimental process data conducted during this phase of the research. Figures 22 through 59 present photomicrographs showing the following.

1 Substrate Preparation - Effects of various cleaning treatments, nickel electroplating, degassing, surface roughness, and edge radiusing on subsequent TCVD deposits (Figures 22 through 25).

2 Joint Geometry - Effects of various specimen joint configurations, unbeveled and Vee-Type beveled, on subsequent TCVD made joints (Figures 26 through 32).

3 Nickel/Nickel Oxide Depositions - Study of the effects of adding controlled amounts of oxygen/moisture to the TCVD nickel with the endeavor being to dispersion harden the pure TCVD nickel with a nickel oxide dispersion (Figures 33 through 37).

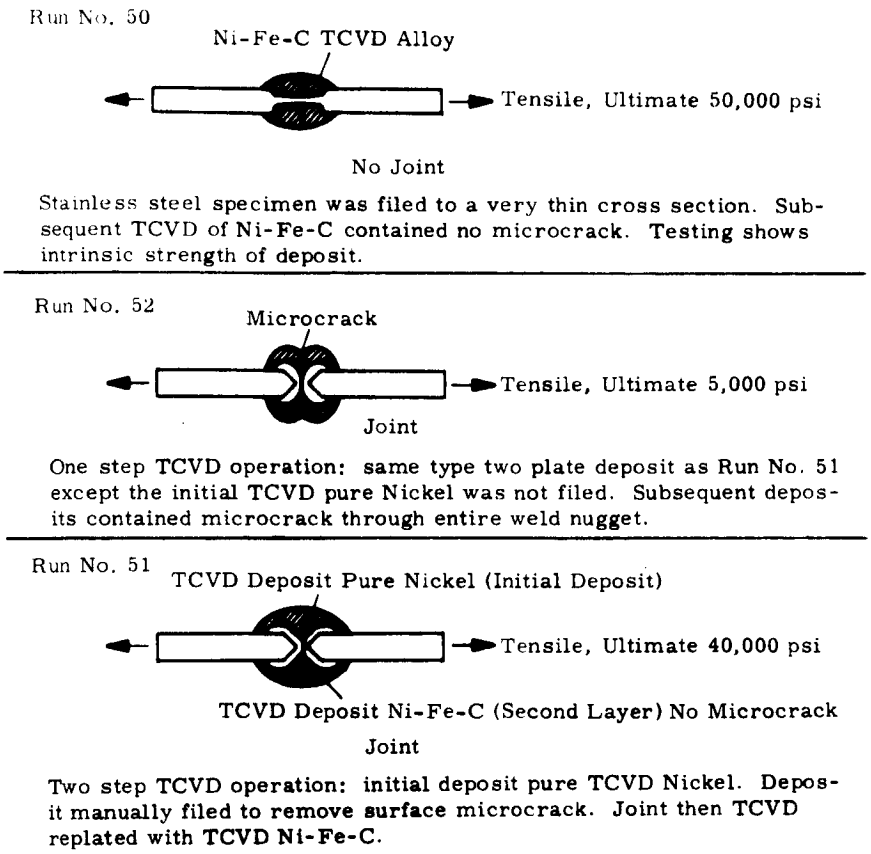


Figure 21. Tendency of TCVD Process in Leaving Microcracks

4 Iron-Carbon and Nickel-Iron-Carbon Alloy Depositions - Study of the properties of Fe-C TCVD depositions; particularly temperatures versus grain size and type. Deposits as such are extremely hard (Rockwell C 60 to 65) and generally unsuitable for TCVD joining due to tendency of Fe-C deposit to spall and exfoliate when coating thicknesses exceeding a few mils Adding Fe-C to the pure nickel by simultaneously TCVD plating with iron and nickel carbonyls does, however, add a very important strengthing mechanism in the development of a structural joint (Figures 38 through 59).

5 Grain Size and Type at Various TCVD Temperature - TCVD temperature study on grain size and type (other process parameters were kept constant). The efficiency of the process as described by Hoyle (Reference 2) depends on temperature and flowrates. Deposition rates were approximately 50 mils per hour, conversions of carbonyls to metal approximately 70 percent at TCVD temperatures of 600 to 800°F. Grain size, shape, etc., were determined by etching substrates with Carapella's Reagent and making microsection enlargements at 75X and 500X.

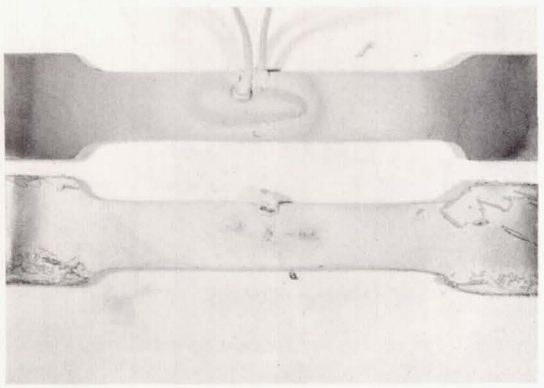
A. SURFACE PREPARATION

Basic Considerations

Evaluate effects of various surface preparations (cleaning, activation, electroplating, degassing, and surface smoothness) on the metallurgical (adhesive) bond of thermochemical vapor depositions (TCVD) to stainless steel substrate (321):

1 Cleanliness - freedom from contamination: organics such as grease and oils; inorganics such as metal oxides of chromium, nickel, and iron together with adsorbed gases such as moisture and air.

2 Smoothness and edge radiusing - substrate effects such as sharp edges, microsmoothness, and microcracks on TCVD microthrowing power.



Note: Figures 22b, 22c, and 22d show results of subsequent tensile testing, i.e. failure of the nickel electroplate to the stainless steel substrate due to inadequate degas treatment prior to the TCVD.

Figure 22a. Dogbone Specimen Used for Evaluation of TCVD Metallurgical (Adhesive) Bone and Intrinsic Strength of TCVD Nickel (3X) (Process Run No. 20)

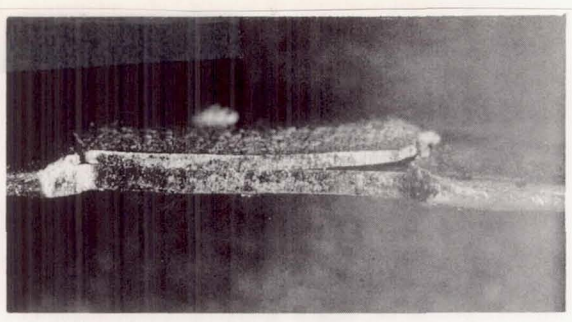


Figure 22b. TCVD Nickel Tensile Shear Failure at Approximately 25,000 psi, 22 Percent Elongation (10X) (Process Run No. 20)

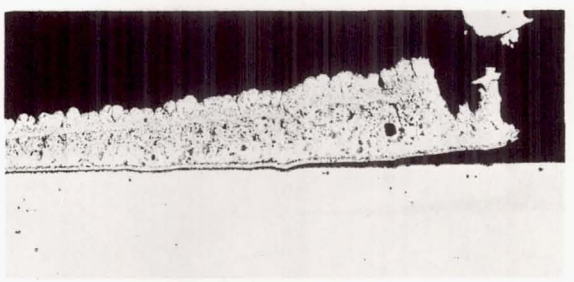


Figure 22c. TCVD Nickel Nodular Deposit and General Failure to Substrate (100X) (Process Run No. 20)

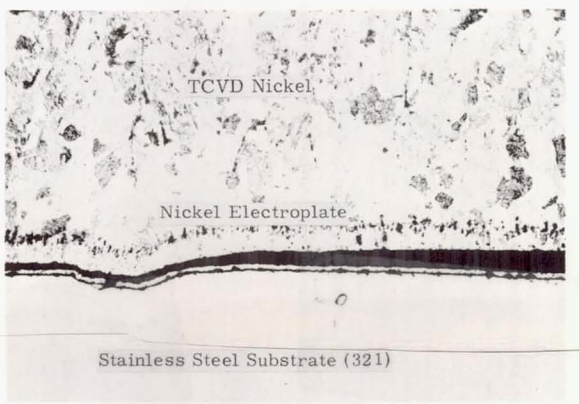


Figure 22d. TCVD Nickel Failure to be Between TCVD Deposit and Nickel Electroplate (500X) (Process Run No. 20)

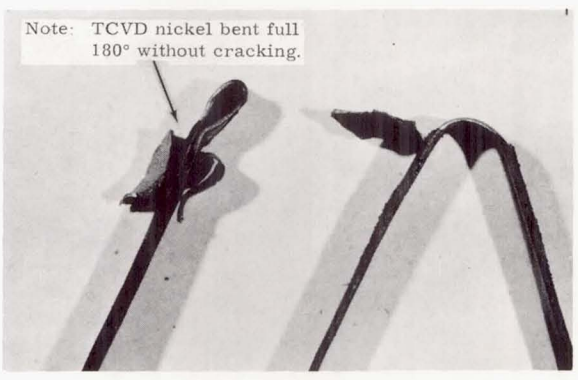
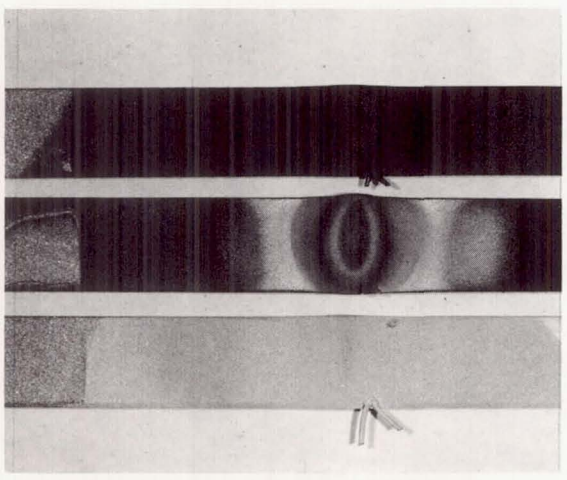
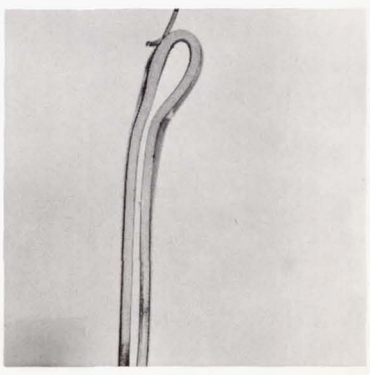


Figure 23b. TCVD Nickel Failure to Stainless Steel Substrate Due to Omission of Degassing Treatment Prior to TCVD (3X) (Process Run No. 31)



Note: Figures 23b and 23c show TCVD nickel to stainless steel substrate failures on 180° bend test due to inadequate degassing treatments prior to TCVD.

Figure 23a. TCVD Nickel Deposited at 400, 600, and 300°F (3X) (Process Run No. 44)



Note: The desired adhesion to stainless steel substrate is shown. (Small ear at top of specimen is clipped thermocouple wire).

Figure 23c. TCVD Nickel Properly Degassed Prior to and Immediately After Initial Deposition (3X) (Process Run No. 44)

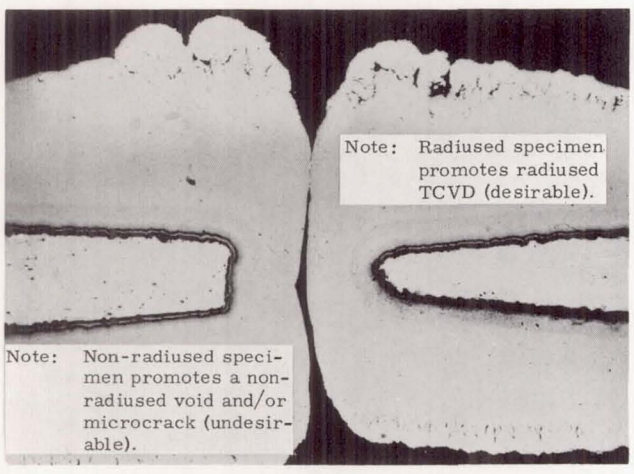
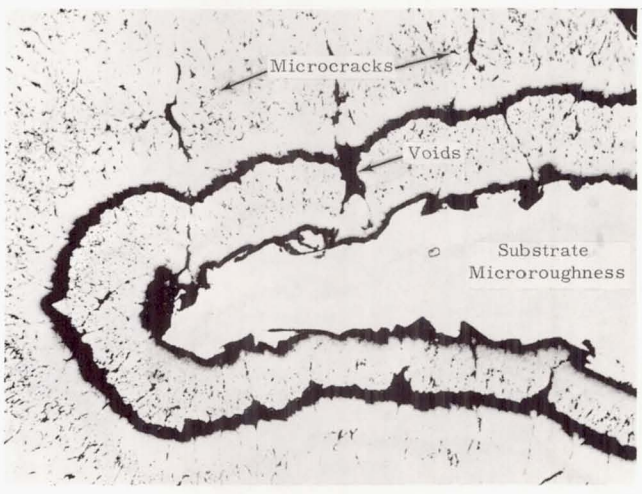


Figure 24. TCVD Nickel Doubled Beveled Vee-Type Joint Showing Adverse Effect of Improper Radiusing with Void and/or Microcrack Propensity (75X) (Process Run No. 40)



Note: From the substrate microroughness eminates voids and microcracks propagating throughout the TCVD deposit.

Note: Note how gross microroughness of the substrate has adverse subsequent effects of the TCVD deposit, i.e. microcracks initiated during initial TCVD deposition continue propagation through the TCVD deposit.

Figure 25. TCVD Nickel Deposited on One Side of a Vee-Type Doubled Beveled Joint (500X) (Process Run No. 35)

B. JOINT GEOMETRY

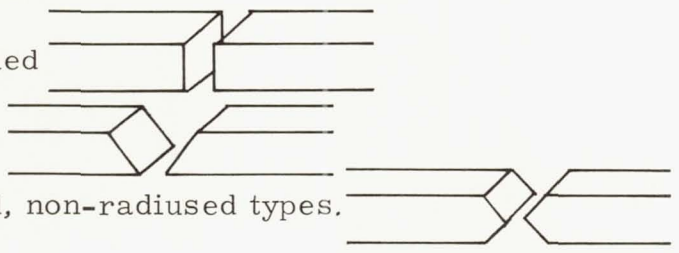
Basic Considerations

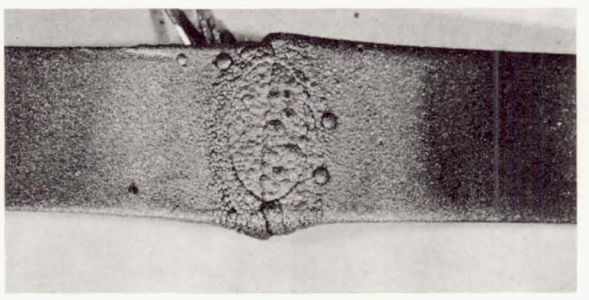
Establish microthrowing power effects of thermochemical vapor depositions (TCVD) on specimen of various joint geometries, for example:

1 Butt joint: square edges, unbeveled

2 Single bevel: vee-type, radiused

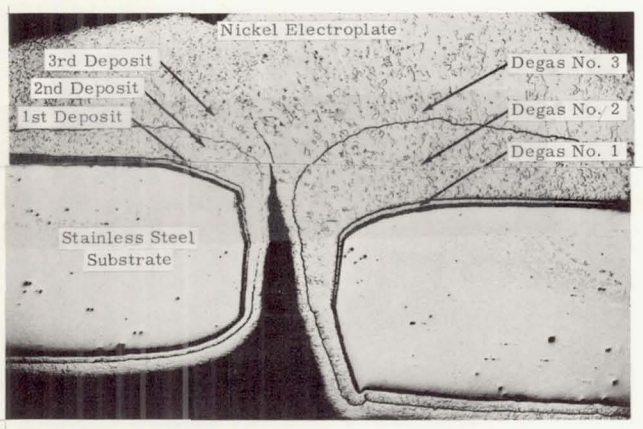
3 Double bevel: vee-type, radiused, non-radiused types.





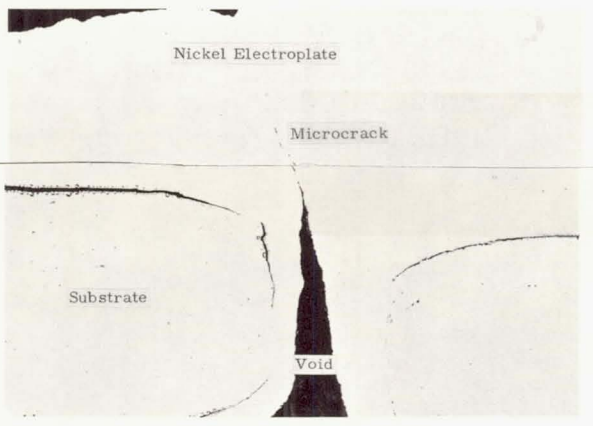
General line of weakness in center, somewhat rough, modular appearance.

Figure 26b. Butt Joint TCVD Weldment (6X) (Process Run No. 22)



TCVD deposit tends to close over the joint area without filling weld zone. Joint when viewed from underside displays void. Void plus microcrack acts as a notch seriously weakening structural joint properties (etched microsection). Note the void appearance (Degas Lines Nos. 1, 2, 3 do not appear on unetched microsection on the right).

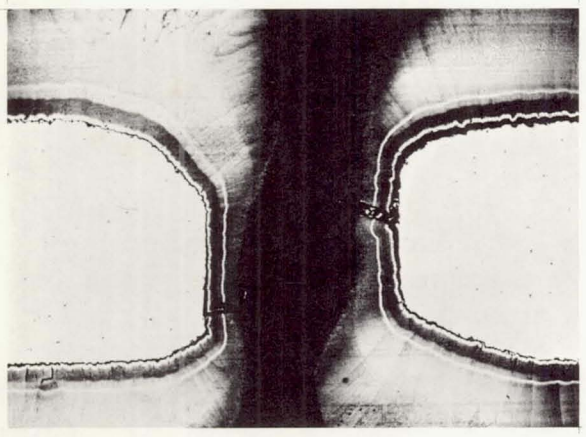
Figure 26a. Butt Joint: TCVD Nickel Deposition on Top Side Only (Single Nozzle) (100X) (Process Run No. 22)



Note 1: Void between the electroplated nickel stainless steel substrate and the first deposit of TCVD nickel.

Note 2: The void appearance lines (Degas Nos. 1, 2, 3) are not true voids, i.e., do not appear on the non-etched microsection thus indicating that these are a high energy phase (probably nickel oxide films from an undesirably high amount of moisture and oxygen contamination in TCVD environment).

Figure 26c. Unetched 100X Microsection of Butt Joint Showing True Voids and Microcracks (Process Run No. 22)



This configuration actually formed a low strength joint but broke during metallurgical mounting.

Figure 27. Butt Joint Nickel Deposition on Both Sides (Double Nozzle) (75X) (Process Run No. 38)

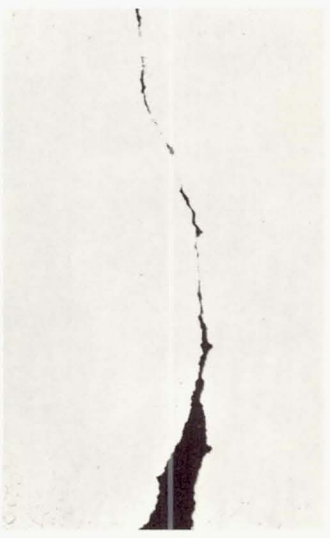
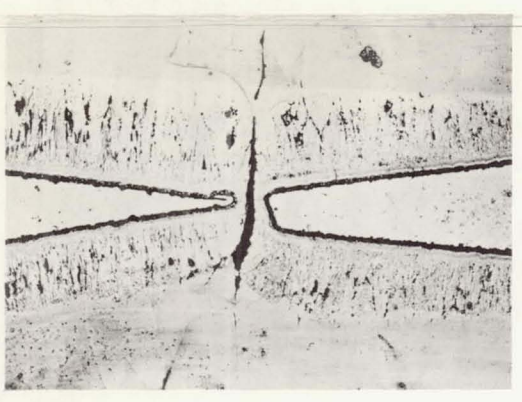
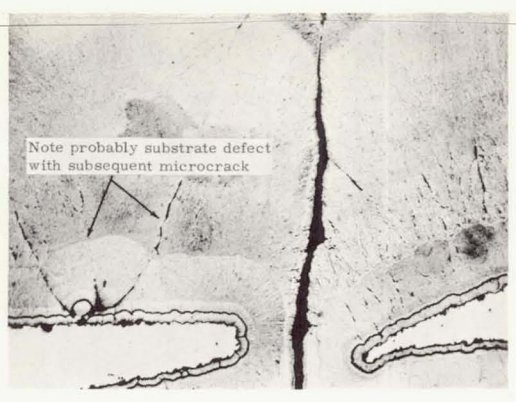


Figure 26d. Unetched 500X Microsection of Butt Joint Showing the Extent of Microcrack Penetration Throughout the TCVD Deposit (Process Run No. 22)



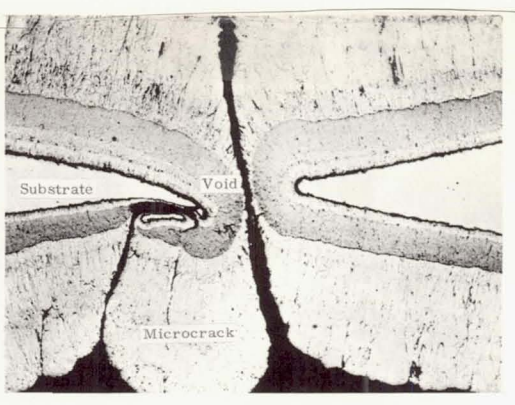
Note: Void-microcrack propensity even with good joint geometry.

Figure 28. Double Bevel, Vee-Type Joint: TCVD Nickel Weldment Deposit on Both Sides (75X) (Process Run No. 39)



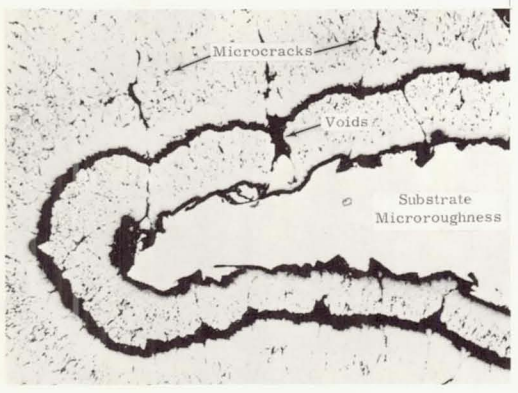
Note: Void-microcrack extending throughout entire weldment.

Figure 29. Double Bevel, Vee-Type Joint: TCVD Nickel Weldment Deposit on Both Sides (75X) (Process Run No. 39)



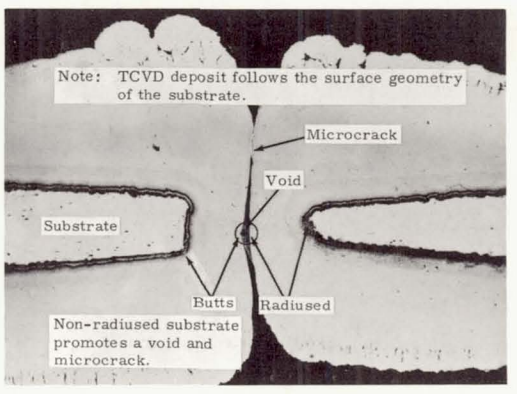
Note: Void-microcrack extending throughout entire weldment. Rough, modular, columnar grain with considerable fine microcracks characteristic of TCVD depositions at high temperatures (>700°F) and high carbonyl flow rates.

Figure 30. Double Bevel, Vee-Type Joint: TCVD Nickel Weldment Deposit on Both Sides (75X) (Process Run No. 39)



This is a repeat of Figure 25 showing the importance of substrate smoothness as a part in optimizing joint geometry tendency of substrate roughness to initiate voids and microcracks in subsequent TCVD deposits.

Figure 31. TCVD Nickel Deposited on One Side of a Vee-Type Double Beveled Joint (500X) (Process Run No. 35)



This is a repeat of Figure 24 showing the importance of substrate radiusing as a part in optimizing joint geometry. Note tendency of left substrate to act similar to the butt welds (Figure 32) in promoting subsequent voids in TCVD. Actual, but low strength joint weldment.

Figure 32. TCVD Nickel Double Beveled Vee-Type Joint Showing Adverse Effect of Improper Radiusing with Void and/or Microcrack Propensity (75X) (Process Run No. 35)

C. NICKEL/NICKEL OXIDE DEPOSITIONS

Basic Considerations

The quality of thermochemical vapor deposited (TCVD) nickel is directly affected by temperature and moisture/oxygen contamination.

1 Temperatures:

a Below 500°F - TCVD nickel deposits are dark and brittle; tending to crack and exfoliate with stress (bending)

b 500° to 650°F - TCVD nickel deposits are banded but less brittle; tending to crack and exfoliate with stress (bending)

c 800°F - TCVD nickel deposits are shiny and ductile and metallurgically (adhesive) bonded to substrate.

2 Moisture/Oxygen Contamination Effects - According to Owens (Reference 11) air leaks (moisture/oxygen) contaminate and adversely harden TCVD depositions. Subsequent carbonyl/air flows TCVD depositions at 800°F produced very rough, nodular deposits, but failed to harden the deposit appreciably. However, at 400°F the TCVD deposit spalled and exfoliated. Normal 400°F TCVD nickel is intrinsically brittle but of sufficient adhesive strength to adhere to substrates unless flexed (see Figures and). Apparently the 400°F TCVD with moisture/oxygen embrittles deposit even further with subsequent increased hardening, internal stress, and exfoliated effects.

Temperature Effects:

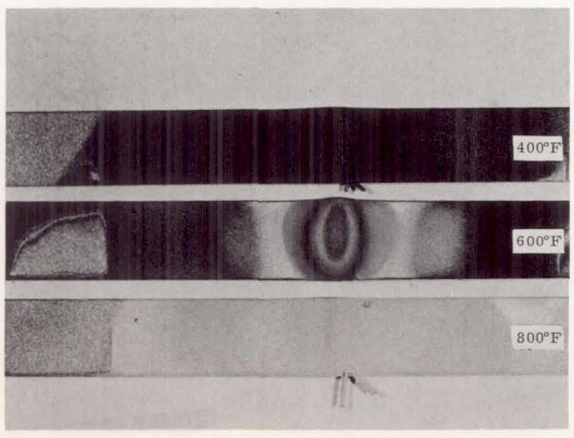
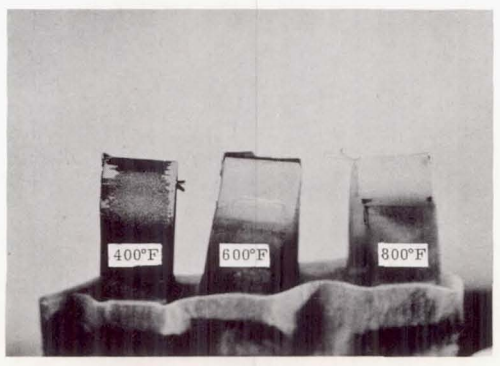


Figure 33. Appearance of TCVD Nickel on Flat Specimens at Various Temperatures (3X) (Process Run No. 44)



Note: Low TCVD temperature effects give a color stratification to deposits on this double beveled Vee-Type joint. Also note effect of substrate surface roughness and microsurface profile on subsequent TCVD nickel depositions. Substrate effects are tremendously magnified as TCVD deposit increases in thickness (75X) (Process Run No. 36)

Figure 34. Specimens Bent 180 Degrees to Illustrate the Brittleness of TCVD Nickel Deposits at Various Temperatures (3X) (Process Run No. 44)

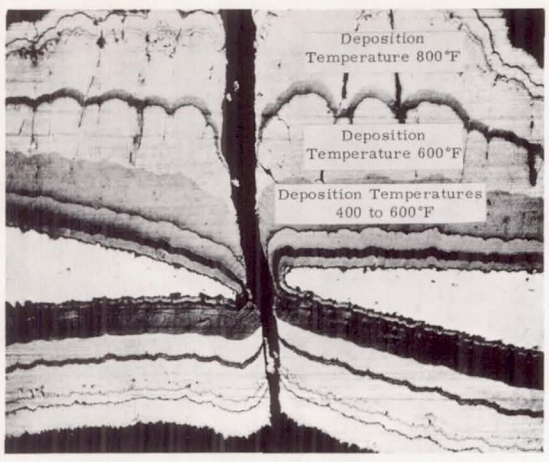
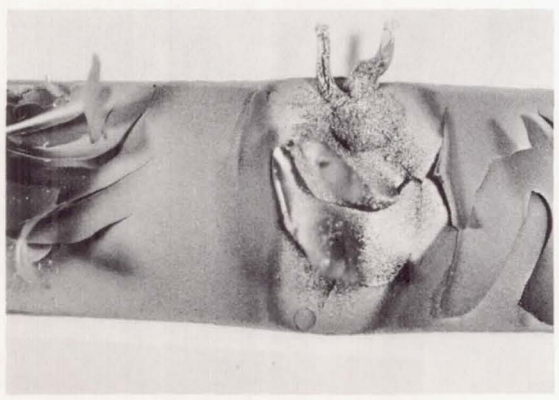


Figure 35. Low TCVD Temperature Effects on Double Beveled, Vee-Type Joint (75X) (Process Run No. 36)

Moisture/Oxygen Contamination Effects:



Note: At TCVD temperatures of 400°F oxygen and/or moisture contamination embrittle the already intrinsically brittle nickel causing depositions to exfoliate and spall.

Figure 36. Contamination Effects at TCVD Temperatures of 400°F (10X) (Process Run No. 5)

Figure 37b. Contamination Effects at TCVD Temperatures of 800°F (500X) (Process Run No. 33)

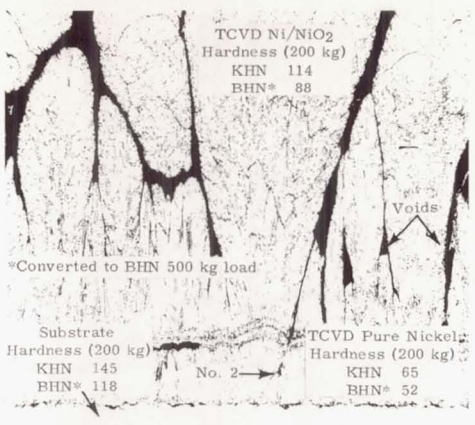
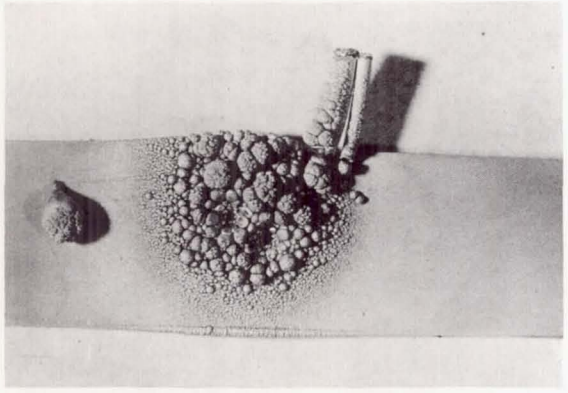


Figure 37c. Contamination Effects at TCVD Temperatures of 800°F (100X) (Process Run No. 33)



Note: At TCVD temperatures of 800°F even large flows of oxygen and moisture did not appear to embrittle the TCVD nickel; however, as can be seen, the deposition became very rough (nodular), completely unsuitable for joints. In the 100X and 500X magnifications note the large number of voids and microcracks extending virtually all the way through the TCVD deposit down to the substrate surface.

Figure 37a. Contamination Effects at TCVD Temperatures of 800°F (7X) (Process Run No. 33)

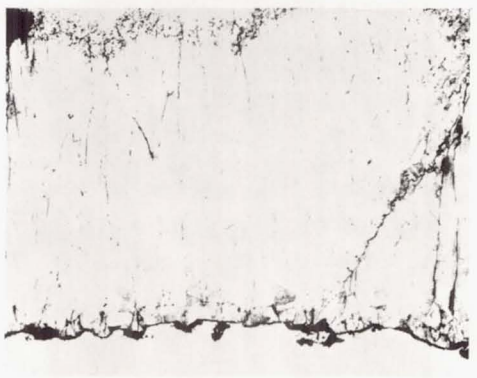


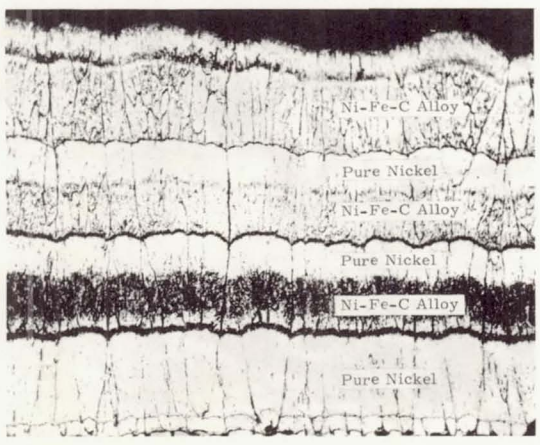
Figure 37d. Contamination Effects at TCVD Temperatures of 800°F (500X) (Process Run No. 33)

D. ELEMENTAL IRON (STEEL) AND NICKEL-IRON-CARBON ALLOY TCVD

Basic Considerations

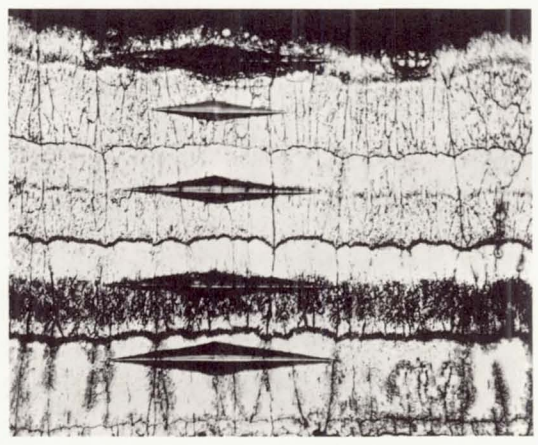
Pure TCVD irons usually contain at least 0.7 percent codeposited carbon, generally making the deposit unsuitable for designs requiring more than a few mils thickness. However by starting with pure TCVD nickel deposits and adding controlled pure TCVD Fe-C deposits (i.e. the carbonyls from each generator are flowmetered, mixed as vapors, and TCVD deposited simultaneously on the stainless steel substrate) a layered effect of pure nickel and various Ni-Fe-C alloy compositions was obtained. Microhardness testing of these layers indicate proper carbonyl process parameters for the subsequent high strength, tough alloy TCVD weldments.

Ni-Fe-C DEPOSITIONS



Note: The initial TCVD plate is pure nickel. Subsequent TCVD plates have alternate layers of Ni-Fe-C alloy and pure nickel deposits. The Ni-Fe-C layers near the top are progressively richer in Fe-C. Note, however, that defects initiating in the first TCVD depositions continue upward, throughout subsequent layers, in a columnar effect, inspite of the following much harder and stronger Ni-Fe-C TCVD deposits. (Apparently proper TCVD principles overrule, i.e., substrate smoothness, joint geometry, etc.

Figure 38. Nickel-Iron-Carbon Depositions (500X) (Process Run No. 41)



Note: Same as Figure 38 showing microhardness indentations testing (KHN 200 kg Load) of the various TCVD pure nickel and Ni-Fe-C alloy deposits.

Figure 39. Nickel-Iron-Carbon Depositions Showing Microhardness Indentation Testing

Fe-C DEPOSITIONS (CARBON APPROXIMATELY 0.7 PERCENT MINIMUM)

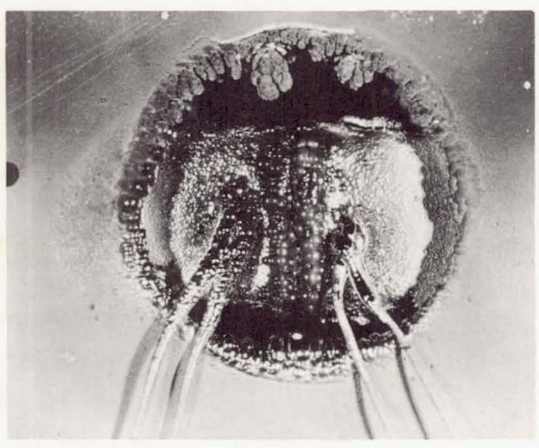


Figure 40. TCVD Iron-Carbon, Double Beveled, Vee-Type Joint Showing Typical Nodular Structures, Thermocouple Wires, and Substrate RF Heating Susceptor (7X) (Process Run No. 6)

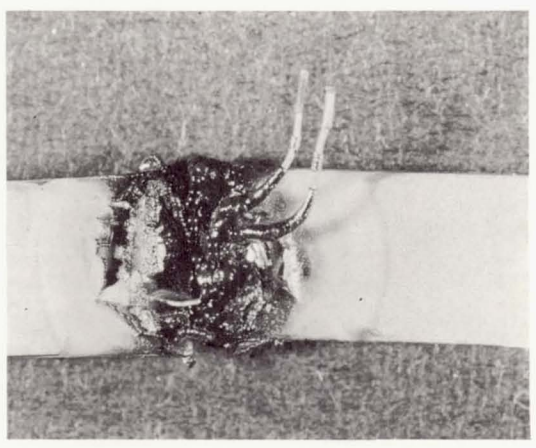


Figure 41. TCVD Iron-Carbon Deposition Showing Tendency for Expoliation and Spalling in Thicknesses Greater Than 0.004 Inch, (7X) (Process Run No. 7)

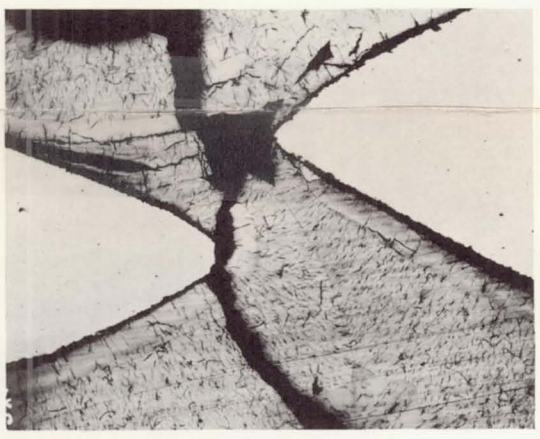
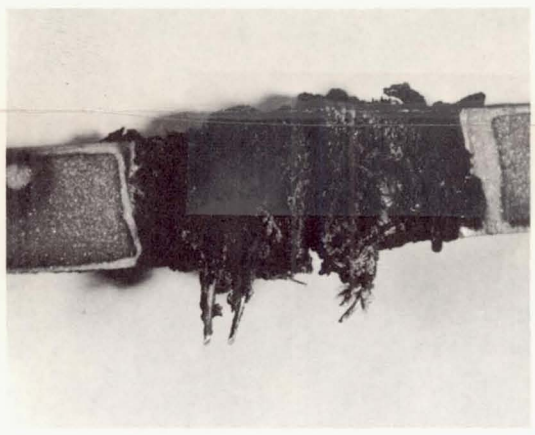


Figure 42. TCVD Iron-Carbon, Double Beveled, Vee-Type Joint Showing Brittle Fracture (75X) (Process Run No. 6)



Note: Deposit consists of mixed Fe, Fe_3C and carbon; crusty, brittle structure (7X)(Process Run No. 2).

Figure 43. TCVD Iron-Carbon Deposit Showing Result of Over-Thermodecomposition of Iron Carbonyl (7X) (Process Run No. 2)

Figure 44. TCVD Iron-Carbon Deposit Showing Iron Rich and Fe_3C Rich Onionskin Layers (2000X) (Process Run No. 6)

Figure 45. TCVD Iron-Carbon Dendritic Trees and Nodules Often Accompanying Thermochemical Decompositions (7X) (Process Run No. 6)

TCVD Fe-C

Basic Considerations

TCVD pure iron deposits from organometallic compounds such as iron carbonyl are invariably accompanied by at least 0.7 percent codeposited carbon. Deposits are extremely hard (Rockwell C Hardness 65) and brittle. TCVD coatings exceeding a few mils tend to exfoliate and spall and are generally useless for weldments. Grain structure and TCVD temperature evaluations however are important in the development of process parameters for the TCVD Ni-Fe-C alloys.

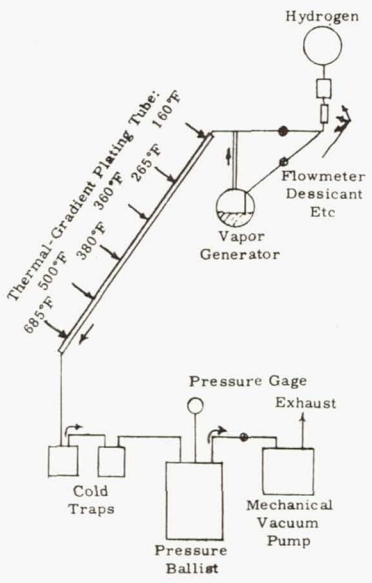


Figure 46. Schematic for Iron Deposition from TCVD of $Fe(CO)_5$

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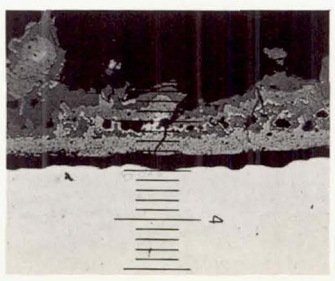
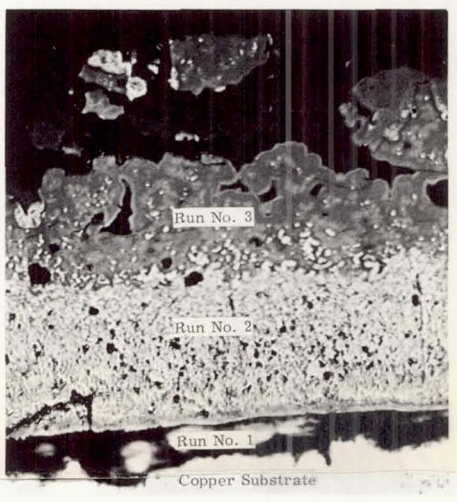


Figure 47. 160°F Iron-Carbon Deposit (250X) (Process Run No. 1)

Note: Poor deposit - Consists of three distinct phases: iron, iron nonocarbonyl (FeCO) and iron pentacarbonyl, i.e., TCVD reaction is only partially complete and gases and liquids are entrapped in the plate.



Deposition Temperature 160°F (2000X)

Note the porosity of the deposit due to entrappment of liquid/vapor iron pentacarbonyl in the deposit.

Figure 48. 160°F Iron-Carbon Deposit on Copper Substrate (200X)

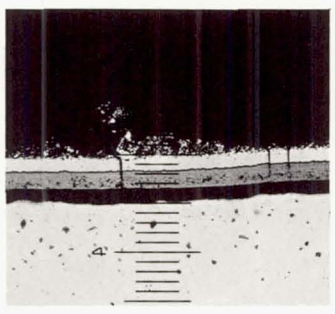


Figure 49. 265°F Iron-Carbon Deposit (250X) (Process Run No. 1)

Poor deposit - Same as 160°F TCVD except note the absence of voids and subsequently less entrapped gases and liquid.

119-2

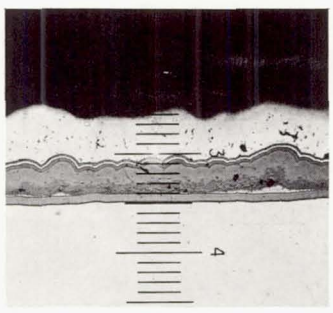
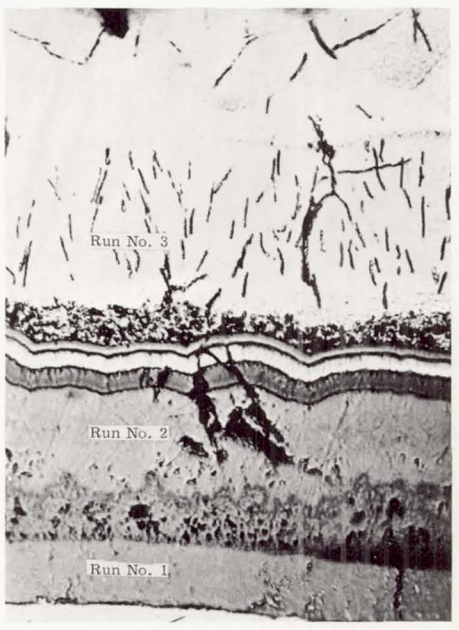


Figure 50. 360°F Iron-Carbon Deposit (250X) (Process Run No. 1)

Better deposit - Thicker deposit ($\cong$ 0.004 inch) with two distinct phases; the gray phase containing higher amounts of free carbon as graphite



Deposition Temperature 360°F (2000X)

Note what appears as a reasonably good deposit at 250X still contains porosity (principally in the Run No. 2 layer) with what looks like free graphite fingers in the Run No. 3 layer.

Figure 51. 360°F Iron-Carbon Deposit (2000X) (Process Run No. 1)

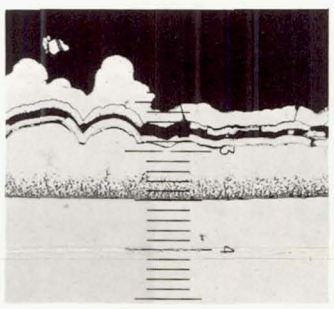


Figure 52. 380°F Iron-Carbon Deposit (250X) (Process Run No. 1)

Best deposit - Less free carbon (graphite). Black layer within the deposit is a spalling crack.

119-3

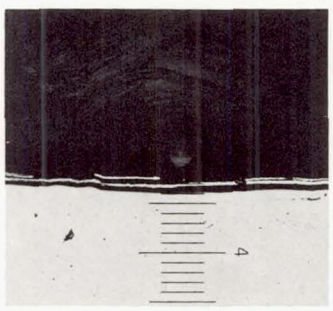
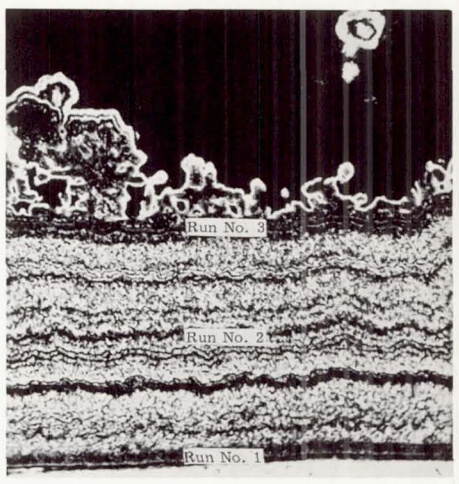


Figure 53. 500°F Iron-Carbon Deposit (250X) (Process Run No. 1)

A good TCVD Fe-C deposit was obtained but broke free from the substrate during metallurgical mounting.



TCVD Deposition Temperature 685°F (2000X)

Note what appears to be a single phase deposit (at 250X magnification) actually consists of stratified phases: a light-colored iron phase; followed by a carbon-rich phase (2000X). (This "onionskin" effect checks with current established literature: "Carbonyl Iron Powder Looks To New Applications", A. Poster, Metal Progress, January 1966, pages 106 - 123.

Figure 55. 685°F Iron-Carbon Deposit (2000X) (Process Run No. 1)

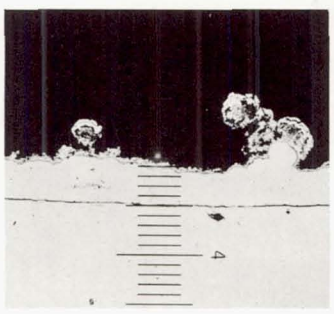


Figure 54. 685°F Iron-Carbon Deposit (250X) (Process Run No. 1)

Best deposit - A homogeneous phase (except for thin plate on surface due to a small amount of TCVD plating during substrate cool down.) No free carbon (graphite)

E. GRAIN SIZE AND TYPE WITH TEMPERATURE

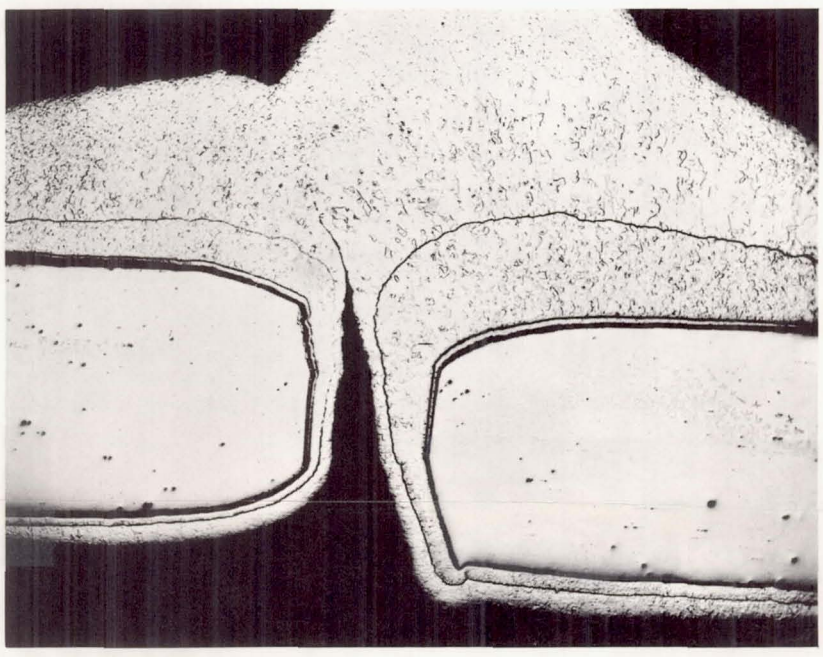
Basic Temperatures

The thermochemical vapor deposition (TCVD) of microstructures free from microcracks is extremely important in the development of deposits suitable for structural welds. TCVD temperatures are basic to grain size, type, density, etc. which in turn affect structure strength. TCVD deposits at various temperatures (keeping all other process parameters constant i.e. vacuum system pressure, carbonyl flowrates, nozzle distance and configuration, etc) were made to determine optimum TCVD temperatures.

TCVD Nickel:

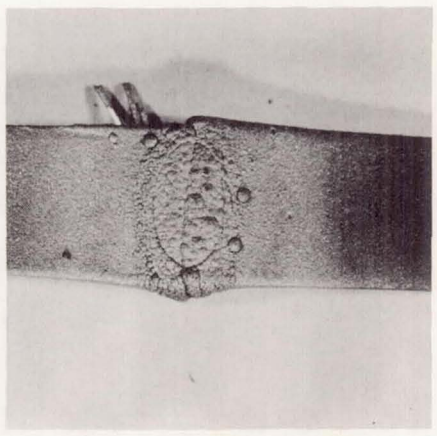
120-1

400°F



Note: Grain appears moderately fine and equi-axed.

Figure 56a. TCVD Nickel at 400°F on Butt Joint (75X) (Process Run No. 22)



Note: Typical nodular development is evident but much less than at 800°F (see Figure 59b).

Figure 56b. TCVD Nickel at 400°F (6X (Process Run No. 22)

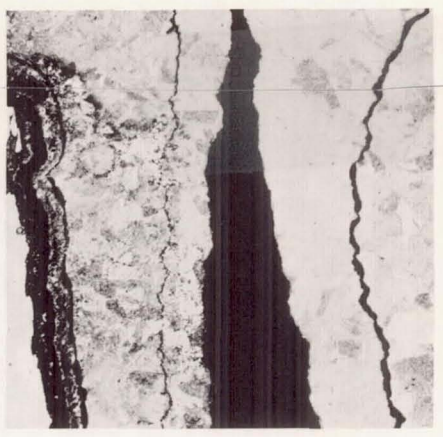
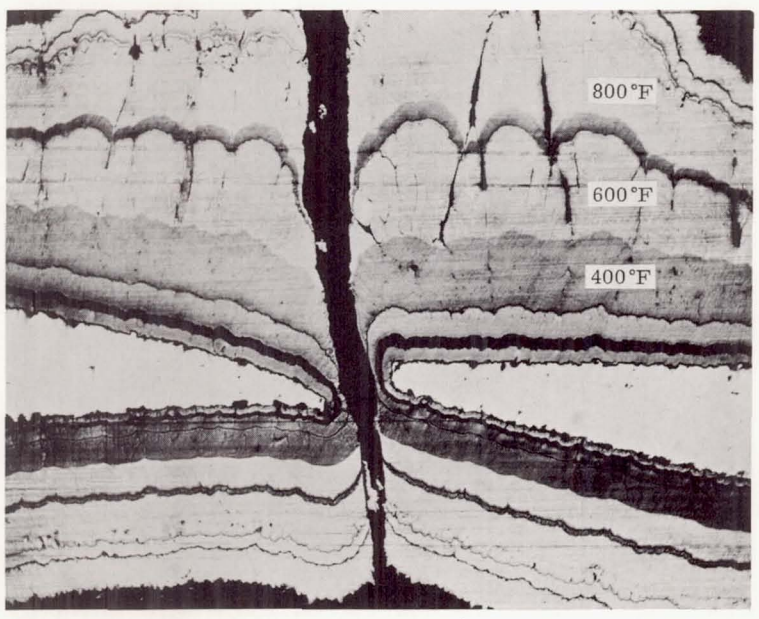


Figure 56c. TCVD Nickel at 400°F Showing Void, Microcracks, and Equi-axial Grains (500X) (Process Run No. 22)

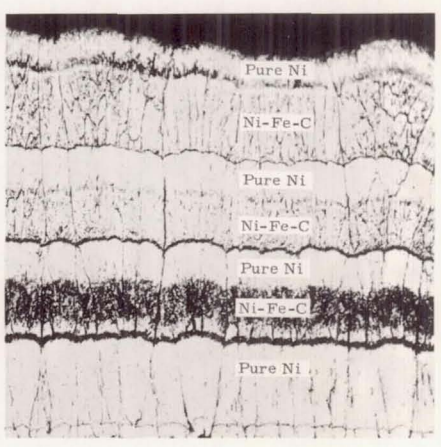
120-2

600°F



Note: Stratifications versus temperature are indicated. Higher magnifications, e.g. Figure 58, show grain structure to be columnar or at least undirectional.

Figure 57. TCVD Nickel at Temperatures of 400, 600, and 800°F (75X)(Process Run No. 22)

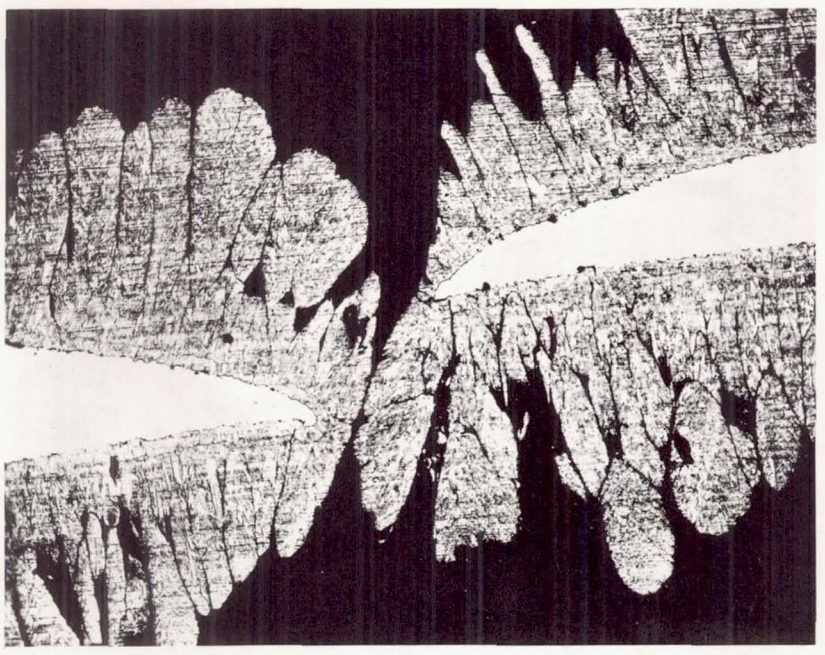


Note: Initial pure nickel (bottom layer has a columnar grain structure) which propagates through all succeeding layers.

Figure 58. TCVD Nickel and Nickel-Iron-Carbon Stratification Layers at 600°F (500X) (Process Run No. 41)

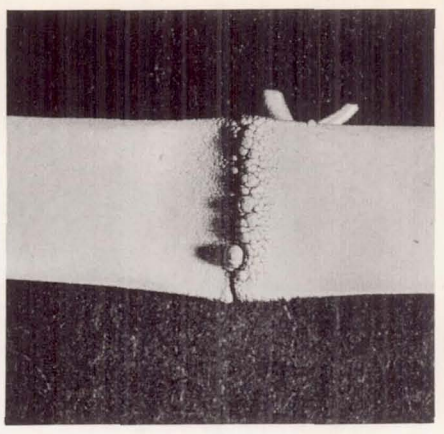
120-3

800°F



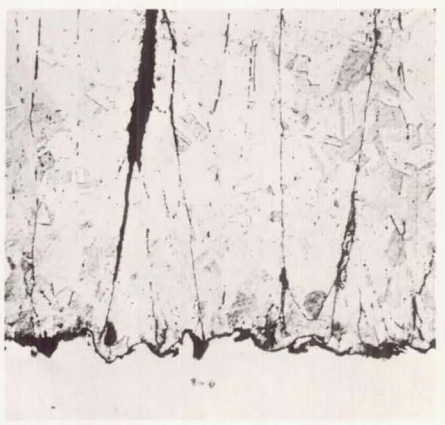
Note: A rough (nodular) deposit insuitable for structure joints is shown. Note the large number of voids and microcracks penetrating to the substrate surface. Nodular deposits of this type are usually caused by premature decomposition of the nickel carbonyl while still some distance from the metal substrate. The liberated nickel atom forms clusters (dust); then impinges on the substrate, leading subsequently to rough deposits.

Figure 59a. TCVD Nickel at 800°F on Double Beveled, Vee-Type Joint (75X) (Process Run No. 37)



Note: Nodules are poorly anchored to substrate being easily broken loose. Deposit unsuitable for joining.

Figure 59b. TCVD Nickel at 800°F on Double Beveled Vee-Type Joint (7X) (Process Run No. 42)



Note: Note the equi-axial smaller crystals, twins, and the long columnar or undirectional crystals extending through the TCVD structure.

Figure 59c. TCVD Nickel at 800°F (500X) (Process Run No. 32)

III. DISCUSSION

The TCVD process shows definite promise for "in-space" fabrication and repair of space structures and orbiting vehicles. The hard vacuums of outer space deleted many of the problems encountered with the process in the earth's atmosphere. For example, oxygen and moisture contamination ceases to be a problem; also, the liquid TCVD plating carbonyls vaporize readily with boiling points less than 50°F. Cleanliness of surfaces to be joined is of a small importance since in outer space surfaces tend to be self-cleaning. The weight and bulk of the TCVD plating carbonyl generator and nozzle required is insignificant; a typical lecture bottle type container being 2 inches in diameter and 14 inches long, weighing only about 3 pounds.

The chief limiting factor in making a TCVD structural joint is the tendency for voids and microcracks to be deposited within the weldment. Vee-type bevels, with radiused edges, greatly enhance the probability of successful structural joints. A much better TCVD joint is possible if the joint can be tacked together with an initial TCVD soft deposit nickel; then sealing the microcrack by peening, filing, etc. The final TCVD of Ni-Fe-C alloy then assures a high strength, tough deposit suitable for use as a structrual joint.

As discussed in Section I, materials selected for fabrication of the TCVD plating system are important only with respect to being vacuum tight. Metals, ceramics (such as glass), and plastics (such as Teflon) are compatible with the TCVD plating compounds. At first, adverse catalytic effects were feared. Particularly with the nickel carbonyl mechanism, interior surfaces quickly became coated with a thin TCVD coating of nickel, essentially nickel lining interior surfaces thereby reducing subsequent possible chemical contamination problems.

The object of depositing TCVD weldments with pure nickel, iron-carbon, and nickel-iron-carbon alloys have been achieved. Merit lies with pure nickel and Ni-Fe-C alloys (Fe-C deposits are too brittle). The nickel/nickel oxide dispersion hardening mechanism did not appear to check out as suggested in the literature by Owens (Reference 11). The Ni/NiO_2 investigation was at TCVD temperatures of 800°F, perhaps too high a temperature i.e. oxygen tends to dissolve in nickel quite readily without forming oxides. The mechanism should be investigated at lower TCVD temperatures.

The Martin Company's approach in these researches has been simplicity and practicality. For example, organometallic compounds (carbonyls) were chosen whereby deposit variations of Ni-Fe-C, elemental or as alloys, could be deposited in a temperature range not adversely affecting the mechanical properties of the stainless steel 321. The equipment consists of standard copper tubing and metal plating chamber, flowmeters (to measure carbonyl vapor flows), moisture traps (desiccants, liquid nitrogen cold fingers), and deoxidizer (palladium catalyst) for helium/hydrogen atmosphere substrate (oxide reducing) hydrogen oxide reduction. Mechanical pumps were used to reduce the plating system pressure to 10 microns (10^{-2} torr). Liquid nitrogen cold traps were used to trap unused carbonyls entering the mechanical pumps (carbonyls are very toxic, sludge pump oils, and increase vapor pressure of the pump oil, limiting vacuum pumping for subsequent process runs).

Conventional cleaning procedures were used in the preparation of the substrate; however, as described in Section I, metals such as aluminum, stainless steel, and titanium rapidly repassivate themselves after cleaning and activating treatments. High temperature oxide reductions with dry hydrogen are not feasible. A better approach appears to be pretreatment of the activated substrate with a metallurgically compatable coating, i.e. nickel electroplate for stainless steel. Oxides of nickel are then easily reduced, during the degassing step, and the subsequent substrate surfaces left in a condition conducive for a TCVD metallurgical bond.

IV. CONCLUSIONS AND RECOMMENDATIONS

High quality pure nickel and nickel-iron-carbon alloy thermochemical vapor deposits have been achieved on stainless steel (321) substrates. Deposition is achieved in a temperature range (500 to 800°F) which does not adversely affect the mechanical properties of the stainless steel.

TCVD joints employing pure nickel and Ni-Fe-C alloy depositions indicated tensile strengths of approximately 40,000 psi. The strength of this deposit can be upgraded well over 100,000 psi through the following straight-forward development:

1 Use of a TCVD plating system with diffusion pump (present system has none) capable of system evacuation to at least 10^{-6} torr (normal good vacuum). The present 10^{-2} torr facility allows oxidation of the stainless steel substrate inspite of the flash nickel electroplating.

2 Development of TCVD process techniques to allow better throwing power of the plating compound into micro-roughness and microcracks. The present system, even with optimum joint geometry, has a tendency to leave a microcrack extending through the entire weld nugget, seriously weaking joint strength. Improvements included:

a Better, non-turbulent carbonyl flows over the joint substrate, i.e. low carbonyl flows and nozzle tilted at an angle to the joint substrate.

b Better methods for sealing microcracks during the initial TCVD deposition. Crude (but effective) techniques include removing the specimen from the plating chamber and manually sealing the initial, soft nickel TCVD deposit by filing, peening, etc. More sophistricated techniques incorporate a small resistance welder (heats locally, not the substrate) which would actually remove the entire microcrack. The smoothened deposit then represents a no-hole surface integrity. Subsequent, final TCVD Ni-Fe-C deposits are then applied. The second Ni-Fe-C deposit is then free of microcracks and is strong and tough, suitable for a structural joint medium. The best method of process improvement would, of course, be the incorporation of a process technique such as an

ultrasonic vibrator which may facilitate TCVD plating penetration into microcracks, crevices, and corners; forming the desireable, dense, void-free structures necessary for weldments.

3 Structural joints, accomplished near the end of this development contract, failed typically at 40,000 psi tensile testing. Weldment compositions were TCVD Ni-Fe-C alloys having a Rockwell C hardness of approximately 32. Future weldments should be made using Ni-Fe-C alloy compositions, at various levels, all the way up to Rockwell C hardnesses of 60 (pure TCVD Fe-C possess Rockwell C hardness 62 to 65). Such harder alloy weldment media could provide structural joint tensile strengths in excess of 100,000 psi and yet display acceptable impact-toughness.

4 Future work should incorporate physical vapor deposition ("vacuum deposition") state-of-the-art techniques i.e. vacuums of 10^{-6} torr, ion bombardment cleaning, baking and degassing in vacuum, etc. Note: Physical vapor deposition is a useful process for applications of pure, (elemental) metals or even layers of different (elemental) metals for use in todays electronics-microelectronics industry. Physical vapor deposition is not, however, suitable due to very poor throwing power (Reference 7) and inability to deposit metal alloys, for structural joint weldments.

Successful TCVD joining should be capable of solving problems in a number of areas (Reference 13).

1 Joining of foamed metals, thin foils, and wires to themselves and to other materials

2 Joining metallic to non-metallic materials

3 Joining non-metallic materials to themselves and to other non-metallic materials

4 Joining of members of small cross-sectional area

5 Joining of fiber-reinforced composite materials

6 Joining of coated materials.

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APPENDIX A

PROCESS DATA AND COMPARISON OF RAW MATERIALS

TABLE I

Nickel, Iron, and Nickel-Iron-Carbon TCVD Process Data*

Run No.	Objective	Process Parameters†	Appearance of Plate	Remarks
1	TCVD iron - determine optimum plating temperature from iron pentacarbonyl $Fe(CO)_5$	Pass iron pentacarbonyl through a thermal gradient copper tube (160° to 700°F)	Less than 350°F - TCVD reaction incomplete, i.e., rough, porous, black plate; 350° to 550°F - gray metallic TCVD plate; 550° to 700°F - black, porous, overdecomposed carbonaceous plate	Process was interrupted and resumed several times to determine subsequent plate adhesions and characteristics, photomicrographs, microhardness, etc.
2	Equipment check out for $Fe(CO)_5$ TCVD plating system	Substrate 500°F, argon carrier gas 250 ml/min, vacuum system pressure 300 to 400 torr	Black - under developed TCVD iron plate heavy, crusty, porous	$Fe(CO)_5$ flowrate much too great, i.e., heat transfer at joint area insufficient for TCVD
3	TCVD depositions at progressively higher vacuum	Substrate 450°F, vacuum system pressure varied from 460 to 160 torr, argon 125 ml/min	Better deposit, magnetic, spalling as TCVD plate thickness increases; black webb-like deposite inside plate chamber and RF coils	Heavy arc and corona problem due to argon, argon free atm - no arcing; CRES oxidation problem
4	TCVD depositions at temperatures suggested in Reference	Substrate 700° to 800°F, argon (250 ml/min) bubbled through $Fe(CO)_5$, TCVD iron with 1600°F H_2 anneal	Black crusty deposit (over thermally decomposed)	"Soot" and webbs all over chamber and RF induction coil - arcing
5	TCVD depositions at the low temperature suggested by Run No. 1	Substrate 360°F, argon 60 ml/min, $Fe(CO)_5$ pressure 360 torr	Good appearance joint (broke during mounting for microstructure); tendency to spall on buildup	Extensive nodular and dendritic growth on CRES susceptor plate; considerable oxidation of juxtaposition CRES areas
6	Repeat of Run No. 5 - a joint was achieved	Same as Run No. 5	Nodular but shiny metallic appearance joint; spalling on underside	Apparently good strength joint but brittle (broke during shear for mounting)
7	Adhesion/cohesion TCVD study - operation at maximum vacuum with no arc/corona using deoxidized hydrogen	Substrate 360°F, no argon, hydrogen (deoxidized) to maintain pressure at 30 torr (<30 torr caused arc/corona)	Accidental temperature overshoot spoiled deposit, i.e., sooty black, crusty	Oxidation of CRES still remains problem (straw yellow oxidation); hydrogen also appears to darken deposit
8	Repeat of Run No. 5 - a joint was achieved; installed palladium cartridge catalyst for hydrogen deoxidation	Same as Run No. 5	Good appearance (color) TCVD but extensive, flower petal type spalling (thickness ≈ 0.004 inch)	Appears TCVD iron deposits are too brittle for use as joint weldments
9	TCVD Ni-Fe-C alloy deposition on CRES flat stock	Substrate 380°F, helium carrier gas bubbled through separate generators of $Ni(CO)_4$ and $Fe(CO)_5$	Good, ductile gray deposit; deposition rate ≈0.011 inch per hour	Deposit probably predominantely Ni due to $Ni(CO)_4$ VP six times greater $Fe(CO)_5$
10	TCVD Ni (100%) ductile, soft	Substrate 380°F, pressure 260 torr, helium carrier substrate material CRES on top, Cu on bottom, degas 420°F for 3 minutes	Good ductile Ni deposit; deposit delaminated on 180 degree bend test; Ni plate extremely soft, ductile; deposition rate 0.014 inch/hour	Surface preparation improvement necessary for metallurgical, adhesive bond
11	TCVD Ni (100%) - attempt to improve bond to substrate	Substrate 380°F, degas at 500°F for 15 minutes, plate 0.0001 inch; degas at 800°F for 15 minutes, pressure 400 torr, He carrier	Thick deposit poor adhesion to substrate (substrate oxidizing, insufficient degassing?)	Nozzle clogging problem i.e., TCVD Ni deposits on inside of nozzle, stopping carbonyl flow
12	TCVD Ni-Fe-C alloy deposition (no carrier gas) - carbonyls flowing through exertion of vapor pressures under vacuum	Substrate 380°F, degas at 800°F for 15 minute, pressure 60 torr, initial plate ≈0.0001, degas again at 800°F for 15 minutes, plate 90 minutes	TCVD deposit of 0.040 inch one side; poor adhesion 180 degree bend test (visible oxidation of substrate interface)	Corona/arc study with air, plant nitrogen, hydrogen, helium atmospheres
13	TCVD Ni - improve deposit/substrate adhesion	Substrate 380°F, degas at 800°F for 30 minutes pressure 1 torr, initial plate ≈0.0001, degas second time at 800°F for 30 minutes, He/H_2 "1", plate 1 hour.	Blue/black appearance deposit, deposition rate 0.060 inch per hour, nodular, crusty, brittle, nonadherent, columnar structure, visible eye	Brittle structure probably due to too low TCVD temperatures
14	Same as Run No. 13 with increased degassing treatments to improve TCVD deposit adhesion	Same as above but with increased degas treatments of 800°F for 60 minutes, He/H_2 flush "1"	Rough, nodular, deposit, gray oxidized appearance TCVD Ni	Substrate heavy oxidized after first degas treatment, thermocouple misreading problem - specimen actually red hot (TC read 800°F), TCVD Ni to 321 substrate failure (bend test)

*Because of the rather large amount of tabulation required to completely define every detail of the Process Run, the general process parameters only are listed. For complete analysis of Process Run refer to Martin Marietta, Orlando, Florida, Engineering Notebooks No. 8983 and 9524 (Engineer: Ralph Wilson)

†Induction heating throughout, double mandrel: above and below specimen except where stated otherwise.

TABLE I (Cont)

Run No.	Objective	Process Parameters	Appearance of Plate	Remarks
15	New equipment checkout - TCVD Ni on nickel electroplated dogbone specimens	Degas at 800°F for 30 minutes, 28 microns, plate 60 seconds (Ni), degas again as before, plate 96 minutes, 300° ± 30°F, single plating nozzle	Blue/black appearance TCVD Ni, turning to good appearance matte, metallic gray, turning back to blue/black appearance during process shutdown; deposition rate ≈0.018 inch per hour	Brittle deposit
16	Repeat Run No. 15	Same as Run No. 15	Run aborted - RF induction field short circuited the thermocouple burning it out	
17,18	Equipment process checkout - dew points of He and H_2, vacuum system pressure (leak) testing, oxidation studies	Martin Company, Orlando, Florida, Engineering Notebook pages 8983 pages 47-59		
19,20	TCVD Ni depositions on nickel electroplated dogbone specimens to evaluate bond and intrinsic strength of deposit	Substrate nickel electroplated from sulfamate bath, degassed at 800°F for 15 minutes, plated for 60 seconds at 400°F, degassed again and plated again for 30 minutes at 400°F, single nozzle	Plate thickness ≈0.020 inch (30 minutes), matte, dull gray appearance	TCVD Ni remained adherent to dogbone specimen, tensile testing to 22% elongation before bond failure to substrate
21	TCVD Ni on nonbeveled butt joint	Joint 0.010 inch gap, SB substrate, nonradiused edge, degas at 800°F for 15 minutes (single nozzle), plate 1 hour, degas, plate 1 hour at 400°F	Joint area filled in with TCVD Ni, evidence of microcrack extending into weld nugget (stainless substrates oxidize during degas treatments)	Low strength joint broke at load of ≈8 pounds, examined fracture - most of area voids or microcrack
22	Same as Run No. 21 except with nickel electroplated stainless steel substrates. Evaluate effects of several additional degas treatments	Joint 0.016 inch gap, sulfamate nickel electroplated stainless substrate, degas at 800°F for 30 minutes, plate at 400°F for 1 minute, degas at 800°F for 15 minutes, plate at 400°F for 30 minutes, degas at 800°F for 15 minutes, plate at 400°F for 70 minutes (single nozzle)	Heavy TCVD Ni deposit on one side, weldment - matte, gray in appearance	Microsection shows extensive microcrack extending throughout the weldment but metallurgical bond to substrate very good
23	TCVD Ni appearance over a range 200° to 800°F	Joint: beveled both sides, nickel electroplated, 0.010 inch gap, degas, plate, degas (same as Run No. 22) followed by depositions at various temperatures (single nozzle)	Deposits at 800°F bright, shiny, matte, 600°F gray, banded, 400°F blue/black, actual low strength joint made; deposition rate ≈0.100 inch/hour	Deposit extremely rough, nodular, joint broke under load of a few pounds
24	TCVD Ni heavy deposits to effect a joint	Joint: beveled both sides, nickel electroplated, 0.016 inch gap, degas, plate, degas (same as Run No. 22) followed by plate at 800°F (single nozzle)	Rapid deposit rate, rough nodular, bright, matte Ni plate	Joint broke during spec cooldown, i.e., coefficient of thermal contraction enough to cause failure
25	TCVD Ni deposition at 800°F	Flat stainless substrate, degas, plate, degas (same as Run No. 22) followed by 45 minute plate at 800°F (single nozzle), loose clamping of specimen in jig	Bright, shiny metallic plate with tending toward rough, nodular growth	
26	TCVD Ni deposit - blue/black brittle deposit investigation, gap geometry	Joint: bevel one side, 0.005 inch gap, degas at 800°F, abort run because of contamination problems (single nozzle)	Black/blue brittle deposits - no joint	Abort run, new copper line and brass fittings somehow embrittled subsequent TCVD deposit
27	TCVD Ni deposit (procedure No. 1 special process procedure to prevent blue/black brittle deposits)	Joint: bevel one side, 0.005 inch gap, degas, plate, degas (same as Run No. 22), plate at 800°F for 30 minutes (single nozzle)	Blue/black brittle TCVD Ni deposit	Joint weldment broke at approximately 10 pounds load
28	TCVD Ni deposit (Procedure No. 1) - continuation of blue/black investigation, gap geometry	Joint: bevel one side, 0.004 inch gap, degas, plate, degas (same as Run No. 22), plate at 800°F for 30 minutes (single nozzle)	Rough, shiny, nodular plate, low strength joint	Gap 0.004 insufficient to allow for 800°F degas (thermal expansion buckling problem)
29	TCVD Ni deposit - repeat of 800°F depositions (Run No. 25), gap geometry	Joint: double bevel, 0.008 inch gap, degas, plate, degas (same as Run No. 22), plate at 800°F for 37 minutes (single nozzle)	Rough, shiny, nodular plate, low strength joint	Joint ruptured on process cooling inspite of loose specimen jigging
30	TCVD Ni deposit, razor sharp hone, joint geometry	Joint: double bevel, 0.000 inch (touching) loose clamping, degas, plate, degas (same as Run No. 22), plate at 800°F	Rough, shiny, nodular plate, low strength joint, no black/blue brittle deposits	Double bevel, double nozzle approach of simultaneous depositions both sides of joint by far most promising approach

TABLE I (Cont)

Run No.	Objective	Process Parameters	Appearance of Plate	Remarks
31	TCVD Ni/O_2 dispersion hardening mechanism study	Flat specimen: degas, plate, degas, (same as Run No. 22), plate at 800°F for 30 minutes; 600°F for 30 minutes using Matheson Co. No. "600" flowmeter for controlled air (O_2/H_2O) carbonyl TCVD depositions	Very rough, nodular, shiny deposit	
32	Same as Run No. 31, except with increased air flow rates	Same as Run No. 31 except with larger flowmeter tube, i.e., "601"	Very rough, nodular, shiny deposit	
33	Same as Run No. 31, except with increased air flow rates	Same as Run No. 32 except with even larger flowmeter tube	Very rough, nodular, shiny deposit	At extremely high air flowrates, TCVD Ni deposit turned black/blue
34	TCVD Ni deposition at 400°F (double nozzle for depositions both sides of joint)	Joint: one side beveled, one side square (butt) degas at 400°F for 5 minutes, plate at 400°F for 5 minutes, plate at 400°F for 60 minutes (double nozzle)	Beveled specimen smooth deposit; square specimen rough, nodular deposit; low joint strength; shiny, matte deposit	
35	TCVD Ni, joint geometry evaluation, 400°F depositions	Joint: double bevel, degas at 800°F for 15 minutes, plate at 400°F for 2 minutes, degas at 800°F for 15 minutes, plate at 400°F for 93 minutes (double nozzle)	Good strength (manual) joint; considerable black/blue problems	Microsection (75X) displays large microcracks extending throughout weldment
36	TCVD Ni - evaluate blue/black depositions to determine where their effects are temperature oriented	Joint: double bevel, degas, plate, degas, (same as Run No. 35), plate at wide range of temperature: 400°, 600° and 800°F	TCVD Ni appearance same as Run No. 23	Microsection (75X) displays various color Ni stratifications; joint (75X) also shows extensive microcracking
37	TCVD Ni - degas and plating treatments at 800°F	Same as Run No. 35 except temperature maintained at 800°F throughout	Good appearance (color) but deposits extremely rough, nodular	No joint, i.e., fell apart during specimen jig disassembly
38	TCVD Ni, butt joint, 400°F deposition	Joint: butt configuration, degas, plate, degas (same as Run No. 35), plate at 425°F for 75 minutes	Heavy deposit but very weak joint strength, i.e., fell apart during jig/specimen disassembly	
39	TCVD Ni deposition 600°F	Joint: 0.008 inch gap, degas at 800°F for 15 minutes, plate at 800°F for 1 minute, degas at 800°F for 15 minutes, plate at 600°F for 88 minutes, He/H_2 "1" flashes (double nozzle)	Good appearance plate until shut down, i.e., black/blue problem (surface only); joint accomplished but microcrack extending through nugget zone	Induction heating tends to give (emf) voltage gradient across butt joint
40	TCVD Ni deposition 400°F with post heat treatment (to improve adhesion to substrate)	Joint: 0.008 inch gap, degas, plate, degas (same as Run No. 39), plate at 400°F for 54 minutes, post heat treatment at 1050°F for 15 minutes	Joint made, dark blue black appearance	
41	TCVD Ni/Fe depositions 600°F	Flat specimen: degas, plate, degas (same as Run No. 39), plate at 600°F starting with pure Ni followed by Ni/Fe deposits increasingly richer in Fe	Smooth appearance plate, Fe additions make deposit darker than pure Ni deposits	Microsection showed laminate layers of pure Ni and Ni-Fe-C with alloy hardness to R_C 48
42	TCVD Ni, thermal "shove together" technique, i.e., specimen ends clamped with subsequent TCVD at progressively higher temperature, thermally expanding joint together	Joint: 0.008 inch gap, degas, plate, degas (same as Run No. 39), plate: start at 400°F, increase temperature slowly ending at 800°F over 90 minute run	Good appearance plate but large crack developed in joint due to thermal contraction on specimen cool down	Specimen requires unclamping at ends at high process temperature to prevent thermal contraction cracking
43	TCVD Ni same as Run No. 42 except with post-heat treatment to remove internal stresses (anneal Ni)	Same as Run No. 42 except added postheat treatment: 960°F for 15 minutes	Good appearance plate, less thermal contraction cracking, appears to be (manually) quite strong	One end of specimen jig unloosed at 800°F to prevent thermal contraction cracking
44	TCVD Ni appearance and deposit ductility (bend testing) at temperatures of 400°, 600°, and 800°F	Flat specimen: degas, plate, degas (same as Run No. 39), plate: specimen No. 1, 400°F; specimen No. 2, 600°F, specimen No. 3, 800°F	At 400°F specimen black blue appearance (brittle); 600°F: gray, banded (brittle), 800°F: shiny, matte (ductile)	
45	TCVD Ni/Ni-Fe-C composite joint: file initial Ni free from microcrack; then Ni-Fe-C top deposit	Joint: 0.004 inch gap, degas, plate, degas (same as Run No. 39), plate at 400°F for 30 minutes; remove specimen, file away microcrack, degas, plate, degas (same as Run No. 39), plate with Ni-Fe-C alloy at 500°F for 45 minutes	Microcrack in initial (Ni) deposit; weld surface free of microcrack, Ni-Fe-C (second deposit) more gray than pure Ni initial deposit but free from microcrack	High strength joint butt broke during weld bead grind down (flush with substrate surface)

TABLE I (Cont)

Run No.	Objective	Process Parameters	Appearance of Plate	Remarks
46	TCVD Ni/Ni-Fe-C composite joint: thermal expansion, "shove together" technique	Joint: 0.004 inch gap, degas, plate, degas (same as Run No. 39), plate: 400°F for 10 minutes, 450°F for 12 minutes, 600°F for 64 minutes (Ni-Fe-C alloy)	No joint, i.e., failed during disassembly from jig; very little TCVD deposition buildup; no nodules, gray deposits	Iron carbonyl TCVD require higher temperature; simultaneous Ni/Fe TCVD apparently requires higher TCVD temperature, i.e., > 600°F
47	TCVD Ni/Ni O_2 deposition 500°F	Flat specimen: degas, plate, degas (same as Run No. 39), plate: 500°F various, controlled, air (oxygen/moisture) flows, simultaneously codepositing with the TCVD Ni	Bright shiny, metallic deposits; propensity toward nodular growth	RF induction heating power failure necessitated an additional 800°F (undesireable) degas treatment
48	TCVD Ni-Fe-C alloy deposit in integral surface, i.e., substrate filed to virtually no thickness (but having no microroughness or cracks)	Flat specimen: filed away cross section, degas, plate, degas (same as Run No. 39), plate Ni-Fe-C 800°F, 650°F, 500°F	Deposit extremely nodular - unsuitable for joints	$Ni(CO)_4$ flowrate too high; filed area of substrate requires radiused edges
49	TCVD Ni Rivet run - evaluated with respect to microthrowing power of plating through holes (lap joint)	Joint: rivet type holes (0.069 inch) drilled in lap joint area, plate, degas, plate (same as Run No. 39), plate at 600°F for 90 minutes with Ni-Fe-C alloy	Cross section of holes considerably reduced on outside (but still present), very poor penetration of TCVD deposit into holes (poor microthrowing power)	Good method for making microsize holes, i.e., start with small mechanical (drill) hole; TCVD deposit decreasing hole to desired microsize
50	TCVD Ni-Fe-C intrinsic strength determination (same as Run No. 48 except polished surfaces, radiused edges)	Same as Run No. 48 except final plate TCVD 600°F for 90 minutes	Good deposit: smooth (no nodules), metallic gray, no microcracks, etc.	Tensile strength of Ni-Fe-C deposit (intrinsic strength) 50,000 psi; specimen cross section removed to virtually zero, all subsequent tensile strength due to TCVD deposit
51	TCVD Ni-Fe-C composite joint, 700°F deposition	Same as Run No. 45 except final plate at 700°F for 60 minutes	Good appearance joint; no evidence of surface microcrack, i.e., within the Ni-Fe-C deposit	Joint tensile strength tested to 40,000 psi; failure not through Ni-Fe-C nugget rather a metallurgical bond failure to the (oxidized) substrate
52	TCVD Ni-Fe-C same as Run No. 51 except microcrack was not filed away in the initial Ni deposit	Same as Run No. 45 except TCVD continuous with no filing away of the microcrack in the initial TCVD Ni	Metallic appearance joint but evidence of surface microcrack in the TCVD Ni-Fe-C deposit	Joint tensile strength tested to 1,000 psi; failure following microcrack interface

TABLE II

Comparison of Vapor Plating Raw Materials
For Iron Deposition

Iron Halides ($FeCl_3$, $FeBr_2$)	Iron Pentacarbonyl ($Fe(CO)_5$)	Dicyclopentadienyl Iron (Ferrocene: $Fe(C_5H_5)_2$)
	Advantages	
Anhydrous, pure, $FeCl_3$, $FeBr_2$ and FeI_2 inexpensive, readily available.	Raw materials, 99.9 percent minimum purity, readily available.	Literature reference as possible organometallic candidate for iron deposition (References 4 and 15).
Straight forward hydrogen reduction chemical reaction.	Straight forward, highly favorable thermodynamic reaction, reported yields to 0.14 inch/hour. Considerable process information available.	Raw materials readily available, easily melted (340°F) and vaporized (480°F). Process equipment and control simplicity.
Potentially high iron (deposition) yield.	Raw material is a liquid; easily vaporized (BP 220°F at 760 mm) and readily decomposed to iron 700 to 840°F: a Equipment simplicity b Substrate not affected by decomposition temperature.	Raw materials and by-products comparatively (to carbon monoxide and halogens) nontoxic.
	Disadvantages	
Anhydrous materials are solids, requiring high process temperatures: $FeCl_3 \xrightarrow[H_2]{\Delta}$ Fe (1200°F) $FeI_2 \xrightarrow[H_2]{\Delta}$ Fe (2100°F) a Eqpt complexity b Affected properties of substrate altered.	Carbon codeposited with iron, usually 0.6 to 1.0 percent. (Deposits subsequently brittle: require process heat treatments in order to build up heavy thicknesses.)	Little information available.
Possible contamination of substrate with unreduced iron halides and halogens.	Deposition currently limited to approximately 15 percent theoretical maximum yield. (Basic problem: Carbon monoxide resulting from reaction: $Fe(CO)_5 \xrightarrow{\Delta} Fe + 5CO$ is strongly adsorped to substrate surface; restricting subsequent depositions (current deposit rates to 0.14 inch/hour).	Subsequent analysis shows material to be extremely thermally stable.
Process information on hydrogen reduction virtually nil (Reference 11)	Carbon monoxide, by-product, toxic.	
Halogen by-products toxic.	Carbonyls toxic.	

APPENDIX B

ANNOTATED BIBLIOGRAPHIES

1. "Prospectus for Research In Molecular Joining," Battelle Memorial Institute, Post June 1964

   Objectives of vapor plating joining are succinctly stated (produce joint in short time, joint strength exceeding the members, reasonable ductility freedom from voids, etc.); followed by a state of the art, comparing electrodeposition and chemical vapor deposition; advantages and disadvantages of commercial processes, and joining problem areas.

   This reference is most relevant as a comprehensive introduction to the subject: vapor plating joining.

2. Sherwood, E. and Blocher, J., "Vapor Deposition: The First Hundred Years," Journal of Metals, pp. 595-599, June 1965

   Review of the highlights of the chemical-vapor deposition process and some of its current applications (years 1864 through 1964). Academic and reference use: 92 references.

   Sherwood, E. and Blocher, J., "Chemical Vapor Deposition - A Tool for Research and Industry," ASM-ASTE Westec Conference, Los Angeles, Calif., Session on Nonmetals and New Processes, March 1964 (see Reference 2 comments)

3. Blocher, J., "Selected CVD Information Developed at Battelle in 1962-1963," Battelle Memorial Institute, November 1964

   Information includes an impressive number of annoted literature references (more than 500) published in years 1961-1963, and also sections on nucleation and growth processes in chemical vapor deposition (CVD) and kinetics of the heterogeneous decomposition of iron pentacarbonyl.

   Extremely good reference for work published in years 1961-1963.

4. Hoyle, Dr. R., "Bibliography and Abstracts: Plating by Thermal Decomposition," Plating, Nov 1962, Dec 1962, Jan 1963, Feb 1963, 352 references

Very good reference article. Bulk of references published 1955-1962. Contains useful "Index of Abstracts of Elements and Compounds by the Process of Thermal Deposition" - a rapid method for locating relevant references for a particular metallic element (Plating Feb 1963, pp. 143).

5. Powell, Campbell, and Gonser, "Vapor Plating," John Willey and Sons, 1955

   Good state of art reference for vapor plating for time period to 1955. Includes vapor plating of metals, carbides, nitrides, boron and borides, silicon and silicides, and oxides. Introduction includes physical property data, coating apparatus, coating characteristics, adhesion, effect of deposition, temperature on properties of coatings, purity of deposits, deposition characteristics, etc.

   Cited references, for iron deposition from the iron halides, did not turn out to be satisfactorily informative.

6. Sherwood, E., "Vapor Plating," Plating, July 1965

   Good basic, introductory paper. Discusses the nature of the process, source of materials, system design, typical temperatures and pressures of operation, deposition rates, throwing power, thickness of deposits, surface preparation, adhesion, size of articles which can be coated, characteristics of deposits, etc.

7. Kaufman, H., "Handbook of Organometallic Compounds," D. Van Nostrand Co., Inc., 1961

   Perhaps the most outstanding collection of organometallic materials available today in one book; iron organometallics, pp. 1523 to 1530.

   Handbook lists name, formula, MW, and physical characteristics. About one-third of materials have a reference. Regretably, this reference is not chemical vapor deposition oriented, thereby limiting its applicability.

8. "Metal-Organic Compounds," Advances in Chemistry Series, 1959

   Various organometallics are analyzed. Many compounds are examined from their thermal decomposition stability. The emphasis of this book is not however on chemical-vapor deposition, hence, its value is somewhat limited.

9. Zeiss, "Organo-Metallic Chemistry," Reinhold Publishing Corp., N.Y., 1960

   This book provides a professional treatment of organometallic chemistry but like reference 8, is not helpful for vapor plating.

10. "Selected Values of Chemical Thermodynamic Properties," Circular of the NBS, U.S. Dept of Commerce, Feb 1952

    Good reference for thermodynamic values for inorganic chemical compounds.

11. Mellor, J., "A Comprehensive Treatise On Inorganic and Theoretical Chemistry," July 1957

    Volume XIV contained the best information the writer could find on the reduction of iron halides for iron deposits; yet process information, i.e., equipment, apparatus, and process controls was completely missing.

    (Emphasis for iron deposition centers on reduction from the natural ores, particularly the iron oxides.)

12. MacNeill, C., "Gas Plating," Metal Finishing, pp. 47-53, February 1964

    Good general reference, i.e., the fundamental principles for selecting gas plating equipment: methods of heating, auxiliary and control equipment and techniques of flow coating, vacuum coating, dip coating, and fluidized bed with typical examples of apparatus designs.

13. "All Purpose Plating Apparatus for Research on Vapor Phase Coatings," ADS-TDR-62-499, September 1962

    Report describes a very fine, precision-type apparatus suitable for elemental or alloy vapor depositions. The merits of this piece of equipment are described, e.g., close control of deposit, physical and chemical structure/properties, experiment versatility, ease of operation, etc.

    Concepts delineated in this report will be incorporated into our apparatus setup.

14. Owen, L. W., "Recent Developments in the Techniques of Nickel Plating from the Vapor of Nickel Carbonyl," Plating, pp. 911-915, October 1963

    Development in the design of equipment by thermal decomposition of nickel carbonyl are described. Nickel carbonyl plates out nickel more readily, and with less problems compared to iron carbonyl plating iron; however the principles developed in the nickel plating hold for the iron also, hence nickel carbonyl plating references will be closely examined especially since nickel plating from the nickel carbonyl has been extensively investigated for specimen size, geometry, mounting techniques, effect of catalytic carrier gases (H_2S) vapor transport equipment, heating of work, etc..

15. Hoyle, R., "Plating by Thermal Decomposition: A Progress Report on Plating System Design and Evaluation," AES Research Project No. 20, 51st Annual Tech Proceedings AES, pp. 30-38, 1964

    Interesting report. Bulk of investigation involved nickel carbonyl, as the plating gas. Suggestion include procurement of chemicals, selection of plating compounds for further study, selection of the plating

method, study methods available and justification of choice, design and construction of substrate and plating chamber, plating system design, analytical method for vapor analysis, parameter evaluation, substrate temperature, flow rate and carbonyl concentration, substrate material evaluation and characteristics of the plated material, kinetic method evaluation, etc.

16. Carlton, H. and Goldberger, W., "Fundamental Considerations of Carbonyl Metallurgy," Journal of Metals, pp. 611-615, June 1965

    Thermodynamics, decomposition of metal carbonyl, surface kinetics, gas phase diffusion, gas-phase kinetics and nucleation: useful reference; particularly because of the emphasis on the iron pentacarbonyl decomposition reaction.

17. Carlton, H. and Oxley, J., "Kinetics of the Heterogeneous Decomposition of Iron Pentacarbonyl," AICE Journal, pp. 80-84, January 1965

    This reference is a continuation and augmentation of Reference 16. Experimental techniques and discussion of experimental results make this reference pertinent.

18. Blocher, J., "Technical Papers Presented at Second Battelle Symposium on Chemical Vapor Deposition," November 1964

    Large volume CVD applications, coatings of hard-metal compounds, nucleation and growth in CVD: the morphology of vapor deposits, pyrolytic carbon and epitaxial silicon, and growth and etching of α-SiC crystals.

    Continuation of Reference 3. This reference is however not applicable to current investigation, i.e., iron deposition.

19. "Metal-Organic Compounds for Vapor-Plating Applications," ML-TDR-64-206, Part I, June 1964

    This is an excellent, up-to-date, report on investigation on above subject. Although not applicable to iron plating, descriptions of plating apparatus, plating procedures, preparation of substrates and carrier gases, are unusually good. Titanium plating (useful for Phase III of our joining investigation) is treated in detail as well as Zr, Hf, Co, Ta, Mo, W, Si and Si-Mo. (Additional quarterly Progress Reports are available through 1964.)

20. "Deposition for the Production of Structure," Contract No. AF 33(657)-7016.

    This program is a series of Interim Progress Reports starting August 1961 and extending through 1963. Purpose of program is the development of material deposition systems (vapor plating is heavily emphasized) capable of producing aerospace components and structures of

metals and alloys known to have serious fabrication limitations. Although reports do not examine iron vapor deposition, the series are valuable particularly with respect to the finer points of apparatus setups; and also because program is slanted toward obtaining heavy deposits (structural fabrication) useful for joining.

21. "Study of the Mechanisms of Pyrolytic Deposition," Tech Report AFAL-TR-65-212, August 1965

    Report not immediately applicable to iron deposition but does however study the physical and chemical factors affecting the deposition of nickel plating from the carbonyl. (As stated previously, iron vapor deposition mechanisms are similar to the nickel carbonyl-nickel plating depositions. Nickel vapor plating information is however relatively plentiful, hence our literature search carries into the nickel carbonyl vapor plating references.)

22. Pirrung, P., "Erosion Resistant Pyrolyzed Ablative Plastics," Part 1. Percusory Materials and Vapor Plating Apparatus, Tech Doc Report RTD-TDR-63-4261, Part I, September 1964

    Report describes substrate preparation criteria of materials selection, thermal processing, and vapor plating of refractory materials, on pyrolized ablative plastics: the objective being to improve the plastics resistance to mechanical erosion and chemical degradation by reactive gas stream environments.

    Report not of immediate value: does however contain some interesting vapor deposition apparatus.

23. Podall, H. and Mitchell, M., "The Use of Organometallic Compounds In Chemical Vapor Deposition," Annals of New York Academy of Sciences, Vol 125, No. 1, pp. 218-228, 1965

    Paper reviews development of chemical vapor deposition since 1955, with emphasis on utility of the organometallic compounds. (Paper of general interest.)

24. Owen, L., "Deposition of Metallic Coatings by Chemical Reaction in the Vapour Phase," Electroplating and Metal Finishing, pp. 296-304, September 1964

    This paper, along with References 1, 6, and 12 are perhaps the best general reference documents on subject of vapor plating.

    The four basic-type chemical equation reaction mechanisms for vapor plating are given: substrate metal interchange, thermal decomposition (inorganics), hydrogen reduction, and organometallic decomposition.

25. Campbell, Powell, Nowicki and Gonser, "The Vapor-Phase Deposition of Refractory Materials: I. General Conditions and Apparatus," Journal of Electrochemical Society, pp. 318-333, November 1949

Although this paper is well done, more recently published references are more informative.

26. Krier, C. and Blocher, I., "Recent Developments in Coatings for Refractory Materials," Electrochemical Technology, pp. 137-147, May-June 1963

Describes developments of vapor plating refractory compounds (silicides, aluminides, oxides, and cermet-type materials onto refractory metal substrate for protection at high temperature atmospheric environments.

Good, current, general interest paper for vapor refractory material coatings. Not applicable to iron vapor plating.

27. Blocher, J. and Oxley, J., "Chemical Vapor Deposition Opens New Horizons in Ceramic Technology," Ceramic Bulletin, Vol 41, No. 2, pp. 81-84, 1962

General paper describing vapor plating coating of ceramic powders using fluidize bed equipment processes. Not applicable to present (iron) study.

28. Cline, J. and Wolf, J., "Vapor Deposition of Metals on Ceramic Particles," Journal of Electrochemical Society, October 1951

Brief paper describing fluidized bed techniques of vapor plating molybdenum, nickel or iron on ceramic particles. General interest only.

29. Oxley, J. and Campbell, I., "Fluidized Beds for Metal Production," Journal of Metals, February 1959

Brief paper describing metal production: dry vapor deposition in a fluidized bed. Seed crystals are introduced into the bed, and are grown by vapor plating for production of metal powders. General interest only.

30. Oxley, J., Hannah, J., and Blocher, J., "Coating Uranium Dioxide Powders with Metallic Tungsten," Industrial and Engineering Chemistry, pp. 1391-1394, November 1959

References 27, 28, 29, 30 were reviewed as general references, particularly with respect to vapor plating material and process equipment selection. General interest only.

31. Powell, C., Campbell, I., and Gonser, B, "The Deposition of Tantalum and Columbium from Their Volatilized Halides," Journal of Electrochemical Society, pp. 258-265, June 1948

General interest only. This reference and also References 32, 33, 34, 36, 37, 40, and 41 were reviewed for process equipment setups in vapor halide reductions. (Initial Material Selection included vapor plating from the halides of iron, requiring temperature starting at 1200°F and extending into the 2100°F region. References provide typical high temperature apparatus setups.)

32. Loonam, A., "Principles and Applications of the Iodide Process," Journal of Electrochemical Society, pp. 238-244, March 1959

    General interest only. See comments Reference 31.

33. Veigel, N. and Blocher, J., "Preparation of Small Samples of Ductile Titanium and Zirconium From the Isotopic Oxides by Iodide Refining," Journal of Electrochemical Society, pp. 647 and 648, July 1962

    General interest only. See comments Reference 31.

34. Owen, L. and Fairman, L., "Deposition of Zirconium Coatings from the Vapour of the Iodides," Transactions of the Institute of Metal Finishing, Vol 39, pp. 98-103, 1962

    General interest only. See comments Reference 31.

35. Wilson, L. and Gregory, N., "Vapor-Solid Equilibra in the Iron-Chlorine System," Journal of Physical Chemistry, Vol 62, pp. 433-437, April 1958

    Paper did not provide any information relevant to the reduction of ferric chloride or to vapor plating of iron.

36. Nash, J., Ogden, H., Durtscki, R., and Campbell, I., "Preparation and Properties of Iodide Vanadium," Journal of Electrochemical Society, pp. 272-275, June 1953

    General interest only. See comments Reference 31.

37. Campbell, I., Jaffee, R., Blocher, J., "The Preparation and Properties of Pure Titanium," Journal of the Electrochemical Society, pp. 271-285, June 1948

    General interest only. See coments Reference 31.

38. Veigel, N., Sherwood, E., and Campbell, I., "Preparation of High Purity Thorium by the Iodide Process," Journal of Electrochemical Society, pp. 687-689, December 1955

    General interest. See comments Reference 31.

39. Trent, D. and Krause, H., "Vapor Deposition of Pure Ruthenium Metal From Ruthenocene," Inorganic Chemistry, pp. 1057-1058, July 1964

General interest only. Paper was reviewed for possible applicability to iron plating from Ferrocene (dicyclopentadienyl iron). Metallocenes in contrast to metal carbonyls offer the advantage of easier handling (less toxic) and eliminate the possibility of metal film contamination by oxides.

Ferrocene, unfortunately, shows considerable thermal stability at temperatures extending somewhat beyond 800°F (although the raw material does show appreciable vapor pressures at lower temperatures.

40. Gonser, B. and Slowter, E., "The Coating of Metals with Tin from the Vapour Phase," (Stannising), International Tin Research and Development Council, April 1938

    General interest only. Process deals with hydrogen reduction of volatised tin chloride. See comments Reference 31.

41. "Fluoride Tungsten," Plansee Proceedings 1964-Metals for the Space Age, pp. 278-300, June 22-26, 1964

    General interest only. Process deals with hydrogen reduction of gaseous tungsten hexafluoride. See comments Reference 31.

42. Powell, C., Rosenbaum, D., Palmer, R., and Campbell, I., "Vapor Deposition of Molybdenum and Niobium Coatings on Stainless Steel Tubes," Battelle Memorial Institute, Report BMI-1228

    This report was reviewed particularly with respect to substrate consideration (stainless steel), i.e., effect of molybdenum and niobium halides and hexacarbonyl vapor deposition reactions, subsequent heat treatments, carbon codeposition (from the carbonyls). This report as such is relevant to current assignment of iron plating from the carbonyl onto 321L stainless steel.

43. Kesler, G., Oxley, J., and Dryden, C., "The Use of Heat and Mass-Transfer Model Studies in the Evaluation of the Rates of Deposition of Metals in Complex Systems," Transactions of the Metallurgical Society of AIME, pp. 9-13, February 1961

    References 43, 44, and 45 are thermodynamically and kinetically interesting but of limited applicability to iron plating. General interest only.

44. Kesler, G., "Factors Affecting the Rate of Deposition of Metals in Thermal Dissociation Processes," Transactions of the Metallurgical Society of AIME, pp. 197-201, April 1960

    See comments Reference 43.

45. Oxley, J. and Blocher, J., "Mass and Heat Transfer During the Chemical Vapor Deposition of Metals "

See comments Reference 43.

46. Hoene, J. and Charles, R., "Thermal Decomposition of Metal Acetylacetonates Mass Spectrometer Studies," Journal of Physical Chemistry, pp. 1098-1101, September 1958

The heat stabilities of nine metal acetylacetonates, in the absence of oxygen, were examined as a function of temperature. The order of increasing heat stabilities based on the evolution of gaseous products, was found to be:

$$\text{Na (I)} > \text{Cr(III)} > \text{Al(III)} > \text{Ni(II)} > \text{Cu(II)} > \text{Fe(III)} > \text{Co(II)} > \text{Co(III)} > \text{Mn(III)}$$

Regretably the paper analyzed the stability of the materials, the analysis of the thermal decomposition being from the gaseous by-products; the nature of the metal deposit unfortunately was not examined or disclosed.

47. Oxley, J., "Diffusion Processes During Chemical Vapor Deposition," Chemical Engineering Progress Symposium Series, Vol 60, No. 48, pp. 54-60, 1964

Gas-kinetics controlling and gas diffusion controlling mechanisms are analyzed, with respect to controlling reaction rates. The analysis is mathematically straightforward. General interest only.

48. Oxley, J. and Oberle, J., "Metal Deposition Coefficients in Filament Bundles," Transactions of the Metallurgical Society of AIME, pp. 927-936, October 1961

Heat transfer rates are measured in a model of a multifilament vapor-deposition bulb for preparation of high-purity metals. Heat transfer coefficients for performance, of large scale, commercial units were determined. General interest only.

49. Tsutsui, M. and Marsel, C., "Investigation of the Preparation of High Purity Metals via the Decomposition of Cyclopentadienyl and Arene II-Complex Compounds," AD 612-074, October 1964

Report investigation for preparation of chromium, nickel, and europium from their organometallic derivatives. Writer was interested in this report with respect to applying this information to the decomposition of dicyclopentadienyl iron (Ferrocene). High purity metal depositions were largely unsuccessful; chromium deposits have substrate to chromium metal removal problems, nickel deposits were contaminated

with carbon; and eropium deposits were not obtained. Report of general interest only; not relevant to vapor plating with the iron organometallics. (No clues on what to expect from the cyclopentadienyl and arene II - complex iron organometallics.)

50. Belser, R. and Youmans, A., "Apparatus for High Rate Sputtering," Plating, pp. 771-774, July 1962

    Reference 50 and 51 are of general interest with applying these techniques in reverse (to the substrate) for purpose of cleaning the specimen prior to vapor deposition.

51. Seeman, J., "Ion-Sputtered Thin Films," Machine Design, pp. 200-209, August 1965

    Comments - see Reference 50.

52. Schladitz, H., "Process and Apparatus for the Metallization of Continuously Travelling of Organic and Inorganic Foils by Thermal Decomposition of Metal Compounds," U.S. Patent 2,789,064, February 1954

    References 52 through 60 deal basically with substrate preparation, vapor plating compounds (usually metal carbonyls) and commercial process equipments for vapor deposition. General interest only.

53. Drummond, F., "Gaseous Metal Deposition," U.S. Patent 2,332,309, May 1940

54. Fink, A., "Carbonyl Metal Plated Product," U.S. Patent 2,682,702, April 1949

55. Toulmin, H., "Method for Hi-Vac Alloying and Coated Product," U.S. Patent 2,685,124, April 1951

56. Oxley, J., "Chemical Vapor Plating Process," U.S. Patent 3,178,308, September 1960

57. Davis, O., "Method for Gas Plating," U.S. Patent 2,763,576, May 1949

58. Fink, O., "Dynamic Pyrolytic Plating Process," U.S. Patent 2,576,289, December 1949

59. Toulmin, H., "Continuous Metal Production and Continuous Gas Plating," U.S. Patent 2,657,457, September 1949

60. Whitacre, J., "Sealing Integral Tanks by Gas Plating," U.S. Patent 3,114,970, January 1959